EXPERIMENTAL
ELECTROCHEMISTRY

BY

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With One Hundred and Thirty Illustrations

NEW YORK

D. VAN NOSTRAND COMPANY

23 MURRAY AND 27 WARREN STREETS

1905

696 99 6

DEDICATED TO

Charles Edward Munroe

AS A TOKEN OF ESTEEM

PREFACE.

It has been the aim of the author to produce a book that will prove useful in both the lecture room and in the laboratory. Although a work upon the subject of electrochemistry must presuppose a working knowledge of chemistry and electricity, it has been the object of the writer to introduce the subject as clearly as possible, dealing with chemistry and electricity without assuming too much on the part of the student. The book is so written that it may be read through as a history by the student, presenting theory and practice together, with the introduction of an ample number of experiments to supply experimental evidence for the theories advanced. In the later and more practical part of the book, exercises in preparing electrolytic compounds and in isolating metals are introduced. It has also been the aim of the writer to introduce new material with suggestions for additional experiments with the hope that the work will not be unwelcome to those already well informed in the subject. Electrochemistry is at best a subject for the advanced student, and in order to carry out the experimental work with profit, as given here, he must have pursued beforehand laboratory courses in both chemistry and physics. If the more mature and experienced student profits by a study of the book, or the instructor obtains assistance in teaching or suggestions for new work, the object in writing the book will be attained.

<div style="text-align:right">N. Monroe Hopkins.</div>

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SOME IMPORTANT SUGGESTIONS TO STUDENTS AND RESEARCH WORKERS IN ELECTROCHEMISTRY.

A PERUSAL of the works devoted to electrochemistry, especially the earlier ones, will show as a rule a sad and almost complete lack of important data relative to practical manipulations. This absence of governing facts in the note-books of many students and research workers also renders it very difficult if not impossible to repeat the work with any certainty, or to instruct others to do so. The author wishes to impress upon the student the absolute necessity of observing and recording numerous electrical factors in all electrochemical work.

Chemists, until very lately, have shown a pathetic need of electrical knowledge, a failing only rivalled, it may be said, by the lack of chemical knowledge exhibited by electricians. It should be constantly borne in mind that electrochemistry is primarily the work of the chemist. The application of the electric current and its control, although of vital importance, is subordinate to the purely chemical side. Electrochemical operations are essentially chemical and based upon purely chemical changes, and it is only the man with a broad and keen insight into theoretical chemistry who can ever hope to make a successful electrochemist or electrochemical engineer. Nevertheless a thorough working knowledge of electricity is to-day absolutely necessary for success. Electrochemical science is only to be mastered by the man with a chemical and physical equipment.

A few words of caution relative to practical work. Do not begin an experiment or a preparation by roughly mixing up an electrolyte and subjecting it to the action of an unmeasured electric current in a haphazard manner. If you enter in your note-books that a solution of a certain strength was electrolyzed for a certain time by

a current of so many amperes, do not feel that you have recorded all the important data. You have not begun to take into account the necessary governing conditions. What of the temperature? What of the electrode area and current density, as well as the material of the electrodes? What was the electrode tension? The specific gravity before and after electrolysis? What was the character of the apparatus and the dimensions of the cell? Were anode and cathode temperatures the same or was there a difference? These are but a few questions that could be asked after an experimental run, all of which throw important light upon what was going on. Let the student have constantly in mind that he is above all things a chemist and doing a chemist's work, and, secondly, that he is a physicist or electrician, and that the electric current which he is using is capable of application in numerous ways. An electric current is composed of factors, and its deportment as a reagent is largely dependent upon these factors. A student who mixes up a solution in a hurry, sticks in electrodes more or less clean, and turns on the current will never get the most out of a possibility except by a remote chance; and if he is a careless worker, he is not likely to recognize the full significance of a success if by chance he should succeed. Some cases of electrolysis are extremely complicated, and it will even prove necessary at times to repeat the same experiment many times in order to obtain and record all the facts. One run may be made for anode and cathode temperature changes, another for density changes, and another for analytical purposes, all with a constant and set current strength, perhaps. Do not feel that one must use large quantities. The best work is often done by repeated experiment, using small quantities of material.

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A review of the historic writings upon electrolysis and electrochemistry, electrometallurgy, etc., to date. The bibliography is not claimed to be in anywise complete, but it is thought to cover many classic writings as well as numerous important researches of a more recent and practical nature. The bibliography as introduced should be of especial value to students interested in early work.

EXPERIMENTAL ELECTROCHEMISTRY.

CHAPTER I.

HISTORICAL NOTES, AND IMPORTANT CLASSIC RESEARCHES, WITH SIMPLE DIAGRAMS OF THE USE OF THE ELECTRIC CURRENT TO ELECTROLYSIS.

BELIEVING that the proper introduction to this volume should give a review of the historical work, together with a notice of the more basic experimental evidence obtained in support of the theories and laws advanced, the opening pages are devoted to recording the more important researches and discoveries.

As this chapter deals jointly with electricity and chemistry, the best place to commence the recording of events is the time when the galvanic or voltaic current was introduced or grafted into chemistry. The history of electrochemistry before the discovery of the galvanic current requires but a brief description. Ages before the discovery of voltaic electricity it had been observed that various metals, by being simply immersed in metallic solutions, became coated with the metal previously dissolved in the liquid.

Thousands of years ago Zosimus mentioned the deposition of bright metallic copper upon iron immersed in a solution of a copper salt. In the year 1752 Sulzer remarked: "If you join two pieces of lead and silver, so that they will be in the same plane, and then lay them upon the tongue, you will notice a certain taste resembling that of green vitriol, while each piece apart produces no such sensation." Becaria demonstrated in 1772 that metallic zinc could be obtained from its oxide by means of a powerful electric spark, as from a battery of Leyden jars. Paetz and Van Troostvik in 1790

decomposed water by passing electric sparks through it by means of very fine gold wires.

Up to the close of the eighteenth century, however, a possible affiliation of electricity with chemistry was not thought of, the second celebrated experiment of Galvani upon the nerves and limbs of recently killed frogs, in 1786, marking the dawn of what is now known as dynamic electricity. As early as 1780 it was observed by Galvani that the limbs of dead frogs contracted violently when hung upon a copper hook in the neighborhood of a frictional electrical machine, at each disruptive discharge of the then known and so-called static electricity. Six years later Galvani obtained the same results with the limbs and nerves of frogs without the agency of an electrical machine, simply by bringing a copper wire joined to a nerve and one of the limbs in contact with a piece of iron. The analogy of these results, although six years separated, caused Galvani to refer the phenomenon to a common agency, namely, electricity. Galvani describes his discovery of what he called "animal electricity" in his famous "De Viribus Electricitatis" of 1791 in the following words: "It is principally found in the nerves and muscles, and its path seems to be from the muscles to the nerves, or rather from the nerves to the muscles by the shortest route, as in the Leyden jar. There is in every part a double electricity, positive and negative, and disjunctive. One exists internally in the muscles, the other externally; so that the muscular fiber acts like a little Leyden jar, and the nerves simply serve the office of conductors." In the year 1792 Alexander Volta discarded the theory given by Galvani; and from the fact that convulsions took place more energetically when there were dissimilar metals in the connecting circuit, instead of only one variety, attributed the electricity to their being unlike, and laid the basis for the contact theory of electricity. In 1792 Prof. Fabroni, of Florence, first suggested chemical action. The following words are from Prof. Fabroni's report to the Scientific Academy of Florence, concerning experiments which he had made with metals which he had immersed in water. He said that he was convinced that "a chemical action had taken place, and that it was unnecessary to seek elsewhere the nature of the new stimulus, that it was manifestly owing to the slow combustion and oxidation of the metal; which combustion must have been accompanied by an attraction of oxygen and by a

disengagement of light and caloric." In 1793 Alexander Volta of Pavia advanced his contact theory of electricity in the Philosophical and Medical Journal of Leipsic, and later, in his famous memoir to the French National Institute, he gives an exposition of his "electromotive apparatus." It is made, he says, writing in 1801 in the above celebrated communication to the National Institute, "in the form of a pile or of a range of cups, and consists in the simple metallic pairs of plates, so arranged as to impel the electric fluid in one particular direction. The zinc is laid upon the silver, the moist pasteboard over the zinc, and so on consecutively." He called the different conducting substances the "motors," and their arrangement a "circle," "in which an electric stream is occasioned, which ceases only when the circle is broken, and which is renewed when the circle is again rendered complete." The power of chemical decomposition of the voltaic "stream" or current was immediately noticed by numerous workers, Nicholson and Carlisle being the first to decompose water by means of such a current of electricity on May 2, 1800, and soon afterward Dr. Henry of Manchester decomposed nitric and sulphuric acid, and also ammonia, by similar means. With the discovery of the voltaic current scientists became occupied with two great questions: First, what is the true principle of the voltaic cell and the source of the electricity? And second, what is the mechanism of electrolysis, or in other words, how does the electric current decompose chemical compounds? Let us take up the question of electro-decomposition first in the present chapter, and discuss the origin of the electric current when we are in a better position to appreciate the various factors.

In 1801 Dr. Wollaston discovered that if a piece of silver in connection with a more positive metal be put into a solution of copper, the silver becomes coated with copper, which coating will stand the operation of burnishing. During the same year Gerboin first noticed the movement produced in mercury during the act of electrolysis.

In 1803 Hissinger and Berzelius discovered that by means of a voltaic current the elements of water and of neutral salts were transformed to the respective polar wires immersed in the liquid; and Cruickshank, about the same time, observed the electro-deposition of lead, copper, and silver upon one of the polar wires (the one con-

nected with the zinc end of the battery) immersed in solutions of salts of those metals, and was thus led to suggest the analysis of minerals by means of the voltaic current.

In 1805 Brugnatelli observed the electro-deposition of gold upon silver when the former was made the negative pole in a solution of "ammoniuret of gold"; he also discovered the electro-deposition of zinc.

The most brilliant and striking proof, however, of the great breaking-down power of the electric current when applied to chemical
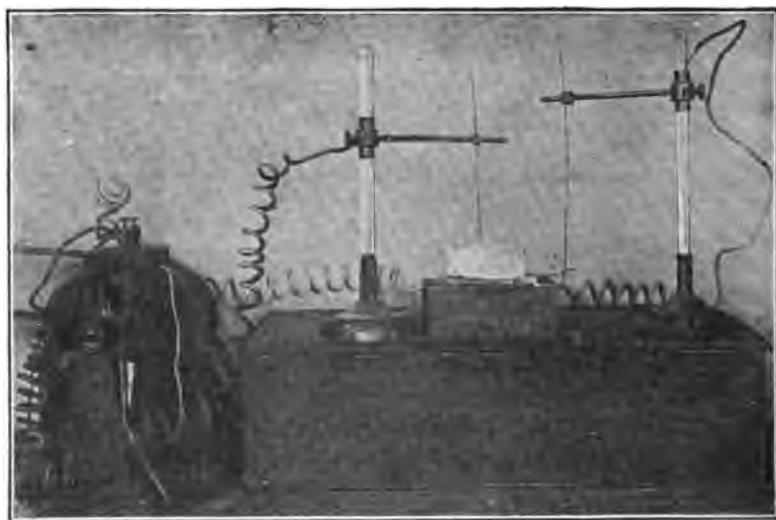
Fig. 1.—Reproduction of Sir Humphry Davy's Classic Experiment in Isolating the Metals Sodium and Potassium.

substances was discovered on October 6, 1807, by Sir Humphry Davy in the electrolytic decomposition of potash and soda, and the liberation of their respective metals, by a current from a voltaic battery of 274 cells.

Let us study this classic experiment, and begin our practical laboratory work by reproducing it, and, under the stimulus of the famous experiment, undertake to explain the mechanism of electrolysis, or in other words, to learn if possible what takes place when an electric current is made to pass through the substances Davy used. First let us look into the actual arrangement of the details of the

experiment. For this purpose we will turn to our illustration. In our electrochemical studies a fair knowledge of chemistry is presupposed, although the author will deal with the subject throughout as simply and as clearly as possible. A small cavity was made in a piece of caustic soda, or sodium hydroxide (NaOH), which was then moistened with water. This was placed upon a piece of sheet platinum connected with the positive wire of a voltaic battery. Mercury was poured into the cavity and connected with the negative wire of the battery, thus closing the circuit through the system.
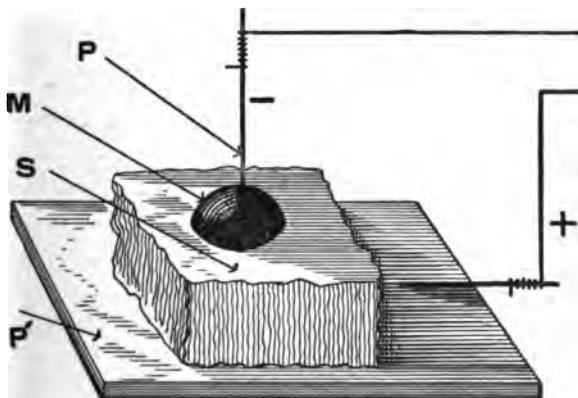
Fig. 2.—*S*, Block of Moistened Caustic Soda or Potash. *M*, mercury in cavity of caustic soda or potash; *P*, platinum wire dipping into mercury; *P'*, platinum sheet for positive-wire connections.

Electrolysis began immediately, the metal sodium, from the sodium hydroxide, being liberated from the hydroxyl and propelled to the mercury, with which it amalgamated. After about an hour, having kept the caustic soda moistened by the addition of water from time to time, the mobile mercury became quite stiff, due to the presence of the sodium amalgamated with it. This experiment can be most easily reproduced, and the sodium be freed from the mercury by distillation of the mercury, leaving the sodium behind, or the amalgam may be put into water, when the sodium will react with the water ($2Na + 2H_2O = 2NaOH + H_2$), setting hydrogen free, which may be ignited, and forming a solution of sodium hydroxide, which may be obtained in the solid form by evaporating to dryness on a watch-glass. In distilling the mercury from the sodium, the reader is referred to any general work on chemistry, where the proper precautions are

given for this operation.   This is a beautiful experiment, and it is strongly urged that every student in electrochemistry repeat it for himself.   In the place of the historic battery of 274 cells, six or eight modern cells of battery will suffice, although the direct current from a lighting system, properly modified by lamps, is to be desired. The use of lighting circuits and lamps for electrochemical processes will be fully dealt with later.   Let us now look into the theory of the breaking up of the sodium hydroxide by the electric current. Davy might have used a strong solution of sodium hydroxide in water placed in a dish, with a layer of mercury at the bottom to act as the negative electrode, and to receive the sodium, and the principle would have been just the same.   Let us represent graphically such a solution, and illustrate by diagram the various steps in the electroly- sis.   As an exposition of all the ancient theories would lead to con- fusion in our practical work, the latest views only upon this subject are given, and we will base our work upon the famous theory of "electrolytic dissociation."   This theory explains in a most satis- factory manner many chemical and electrochemical phenomena, which without its aid would be hopeless.   This celebrated doctrine was advanced by Svante Arrhenius in 1887, and although there are many chemists, physicists, and physical chemists who do not accept it, they have not advanced anything better to account for the numerous things it explains.   There is the most excellent experimental evi- dence in support of this doctrine, which will be taken up in detail later on.   For the present we will assume it to be true, for besides being a theory of exceptional beauty, it will be of great assistance to us in all our work in electrochemistry.   The theory simply states that the molecules of certain chemical substances, when dissolved in water, break up into ultimate parts, and that these ultimate parts carry upon them small charges of electricity.   Let us look at the matter from a diagrammatic point of view.   The accompanying illustration (Fig. 3) shows a series of vessels in which we will electro- lyze a solution of potassium hydroxide.   A represents two molecules of potassium hydroxide about to be plunged into the vessel of water. Here the familiar molecular chemical formula of the base is given. B shows what is supposed to take place according to the theory of electrolytic dissociation.   The potassium atom breaks away from the hydroxyl group, and takes upon itself a charge of positive electricity,

and the hydroxyl group takes upon itself a charge of negative electricity. .All this is believed to happen simply upon dissolving in the water, with no electrical influence whatever being brought to bear.   Here we have, according to our theory, free potassium detached, and isolated from the hydroxyl radical, floating around independently in the water, but covered with a charge of electricity.   At first sight of such a diagram the majority of chemical readers would say that they did not believe a word of it, for in the first place we could not have free potassium floating about in water without a violent reaction taking place between it and the water; and in the second place, where did the charge of electricity come from?. Let us not attempt to answer these questions for the present, but accept the truth of the theory for the time being, and take up the next step in the electrolysis.   In C we have introduced into the vessel two electrodes, one positive and the other negative, as they are connected to the positive and negative ends of a voltaic battery respectively.   We know from our elementary physics and electricity that charges of like signs repel, and those of unlike signs attract.   In this case, if the ultimate parts of the molecule of potassium hydroxide carry positive and negative electrical charges respectively, there should be an attraction between the negative charge of one electrode and the positive charge of the potassium on the one hand, and an attraction

Fig. 3.—A, two molecules of potassium hydroxide before immersion in water; B, the same molecules broken down into "ions" on being dissolved; C, the "ions" being attracted to electrodes of opposite polarity; D, "ions" arrived at the electrodes ready to give up their charges; E, the electrical charges neutralized, the "ions" become atoms and react to form potassium hydroxide again, and water, and setting free oxygen and hydrogen gas.

between the positive charge of the other electrode and the negative

charge on the hydroxyl group on the other hand. If all this is true, there will be a movement of the potassium toward the negative electrode, and a movement in the other direction of the hydroxyl group toward the positive electrode, as indicated by the small arrows in the diagram. These ultimate parts of molecules are called "ions," whether they consist of a single atom, like our potassium with its electrical charge, or whether they consist of a group of atoms, like our hydroxyl, with its electrical charge. Let us then adopt the technical term, and speak of the potassium hydroxide molecule as breaking down, in the presence of water, into a positive potassium ion and a negative hydroxyl ion. The next diagram, D, shows the potassium ions arrived at the negative electrode and, the hydroxyl ions arrived at the positive electrode. We may think of the electrical charges upon these ultimate parts of the molecule as having a protective action, that is to say, rendering them inert so far as the water is concerned. We know that we could not put ordinary metallic potassium into water without a violent reaction taking place, with the liberation of hydrogen and the formation of potassium hydroxide.. Now let us account for the passive state of the ion potassium in the water to be due to the protective action of the electrical charge. What happens when this ion reaches the electrode? We have plenty of negative electricity there with which to neutralize the positive electricity upon the potassium, and neutralization quickly takes place. The diagram E shows the next step; there the electrical charges have been neutralized and removed, and instead of ions we now have ordinary chemical atoms and groups of atoms. In the lower left-hand corner of this last diagram two molecules of water have been graphically inserted; for as soon as the potassium ions become atoms, we know as general chemists that there will be a reaction to form potassium hydroxide, with the liberation of hydrogen. The water was not represented in the previous diagrams simply because it played the part of solvent only, and did not combine chemically with our ions. The arrows here indicate the setting free of two atoms of hydrogen at the negative electrode, and the formation of a molecule of water at the positive electrode, and the setting free of one atom of oxygen. Now, what are the facts in an actual experiment? If we electrolyze a solution of potassium or sodium hydroxide in water, we will have two volumes of hydrogen set free at the negative electrode, and one volume of oxygen at the positive

electrode. If our negative electrode consists of mercury, as in Davy's experiment, the sodium or potassium will amalgamate with the mercury, which prevents it from acting upon the water so long as the current of electricity continues to pass. In the experiment with the block of caustic soda or potash there would be only sodium or potassium set free in the mercury, and oxygen at the moist surface of contact of the caustic block and the platinum-sheet base.

To electrolyze such a solution experimentally, set up an apparatus like that shown in the next illustration. Two large test-tubes may be used, and it will be observed that just twice the volume of hydrogen
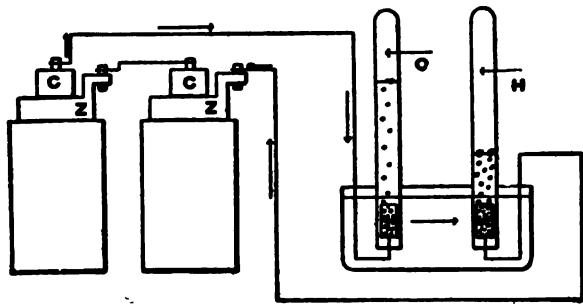
Fig. 4.—Experimental Electrolysis of Sodium or Potassium Hydroxide Solution. *O*, oxygen collected in positive tube; *H*, hydrogen collected in negative tube; *CC*, carbons of battery; *ZZ*, zincs of battery. Arrows indicate the direction of current.

will be set free; in other words, two volumes of hydrogen to one volume of oxygen will be liberated. Where the wires dip under the caustic solution it will be necessary to insulate them with a solution of rubber, or else several coats of gum shellac, to prevent the liberation of gases from the wires themselves. With the ends properly insulated, the setting free of the oxygen and hydrogen will be confined to the platinum plates within the tubes. Now, these platinum plates or electrodes have technical names, and we must become familiar with them. The positive electrode is called the "anode," and the negative electrode is called the "cathode." The current in an electrolytic bath always flows from the anode to the cathode, all electropositive ions going to the cathode, and all electronegative ions going to the anode. As a general rule, all the metals and hydrogen go to the cathode in an electrolytic cell, and all other chemical elements go to the anode. The following table shows the chemical elements arranged in their electrochemical order, some of the extremely rare ones not being included. In this table each chemical element is positive to any

element placed above it, and negative to any one given below it. These distinctions, although of a relative character, are very important, since it seems probable that the very nature of chemical attraction itself rests upon these electrochemical relations.

Anode or Positive Electrode
+

Negative Atoms
{
Oxygen
Sulphur
Nitrogen
Fluorine
Chlorine
Bromine
Iodine
}

Positive Atoms
{
Selenium
Phosphorus
Arsenic
Chromium
Vanadium
Molybdenum
Tungsten
Boron
Carbon
Antimony
Tellurium
Tantalum
Columbium
Titanium
Silicon
Tin
Hydrogen
Gold
Osmium
Iridium
Platinum
Rhodium
Ruthenium
Palladium
Mercury
Silver
Copper
Uranium
Bismuth
Gallium
Indium
Germanium
Lead
Cadmium
Thallium
Cobalt
Nickel
Iron
Zinc
Manganese
Lanthanum
Didymium
Cerium
Thorium
Zirconium
Aluminum
Scandium
Erbium
Ytterbium
Beryllium
Magnesium
Calcium
Strontium
Barium
Lithium
Sodium
Potassium
Rubidium
Cæsium
}

−
Cathode or Negative Electrode.

The above column of elements is arranged seriatim as if placed in an electrolytic cell.

This table very forcibly illustrates the preponderance of positive elements over negative elements, and also the fact that we only have about seven simple negative ions. By a simple ion, a single charged atom like our $\overset{+}{K}$ is meant; a complex ion being one like $\overset{-}{OH}$, which is negative. Here we have a negative atom and a positive atom, composing a negative ion. In this negatively charged hydroxyl group, or hydroxyl ion, we can think of the hydrogen striving to go to the cathode, and the oxygen striving to go to the anode, and the oxygen having the greatest pull and winning, since it is more strongly electronegative than the hydrogen, is electropositive, as a glance at the table will show. By means of this table we should be able to pre-determine the polarity of a complex ion with facility.

For example, let us take the three acids, hydrochloric, sulphuric, and nitric, and disolves them in water. How do they ionize? With the help of the above table and carefully conducted experiment it is an easy matter to determine. The HCl gives $\overset{+}{H}$ $\overset{-}{Cl}$, the H_2SO_4 gives $\overset{++}{H_2}$ $\overset{-}{SO_4}$, and the HNO_3 gives $\overset{+}{H}$ $\overset{-}{NO_3}$. Sulphuric acid has been shown by the present writer to also ionize into the ions $\overset{+}{H}$ $\overset{-}{HSO_4}$. Here we have a case where hydrogen goes to the positive electrode or anode, but it is drawn there by being linked to two more power-fully electro-negative atoms. There are a few cases where metals go to the anode in electrolysis, but only under such circumstances as the hydrogen. No metal goes to the anode in an electrolytic cell, unless it is part of a powerful group of electro-negative atoms. Now if we accept the theory of electrolytic dissociation, we are led to believe in a number of things. Perhaps the most important conse-quence of such a theory is the fact that we have actually moving masses of matter in a solution when an electric current is made to flow through it. Such a solution of a chemical substance, capable of conducting the electric current, is technically known as an elec-trolyte. In all electrolytes, therefore, the passage of an electric current through it is accompanied by the movement of ponderable particles of matter; in other words, the atoms themselves act as carriers of electricity. There will be an abundance of "experimental evidence" later to show this, but for the present we must accept the theory upon faith. As we shall deal a great deal with anodes and

cathodes, and the direction of the electric current, together with its management and application, the latter part of the present chapter will be devoted to the more practical side of the question.

SIMPLE DIAGRAMS OF THE USE OF THE ELECTRIC CURRENT FOR ELECTROLYSIS.

Direction of the Electric Current.—As we must always know the direction of the electric current in all our electrolytic investigations, it does not seem out of place to introduce at this time a purely electrolytic pole-finder, or current indicator. This consists of a glass tube with the ends bent up as shown in Fig. 5, and supported horizontally by a couple of laboratory stands.
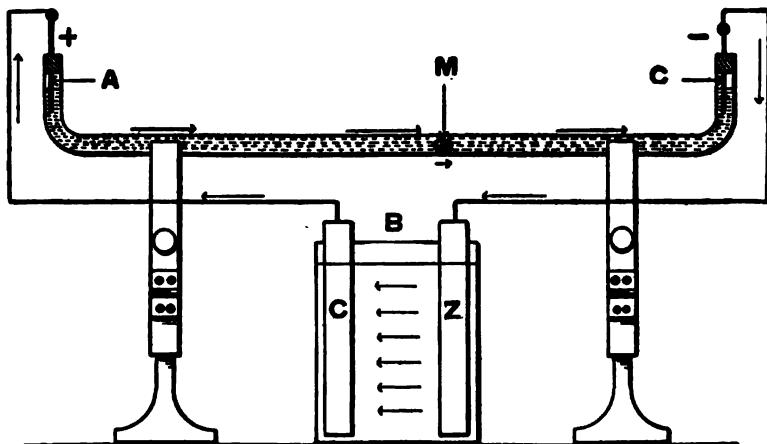
FIG. 5.—*A* and *C*, anode and cathode, respectively, in glass tube; *M*, globule of mercury which travels with the current; *B*, cell of battery supplying current; *C* and *Z*, copper and zinc electrodes of battery. The arrows indicate the direction of flow of the electric current, as well as the movement of the mass of mercury.

Two loose-fitting stoppers carry the platinum-wire electrodes connected to a battery, or modified electric-light current, or small dynamo. A globule of mercury is placed in the tube as indicated at *M*, and the tube filled to near the level of the stoppers with a dilute solution of sulphuric acid in water. Upon closing the circuit, the mercury will immediately travel to the negative pole or cathode. On reversing the direction of the current, the globule of mercury will be propelled in the reverse direction, serving as a very pretty illustration of the behavior of positive ions, and answering all the requirements of a pole-finder or indicator of current direction,

if the current is sufficiently strong.   If the mass of mercury is large
it will require a stronger current to move it, but if quite small it
will be propelled by about $\frac{1}{10}$ of an ampere.   For very feeble cur-
rents, the direction of flow must be learned by means of a compass-
needle.   Perhaps for all ordinary work there is no source of electrical
current so handy and satisfactory as the modified electric-lighting
current when of the direct type, and from 110 to 220 volts pressure.
The accompanying diagram, Fig. 6, indicates the use of such a cur-
rent in connection with an electrolytic cell and a lamp-bank, which
may be placed in any convenient part of the laboratory or workroom.
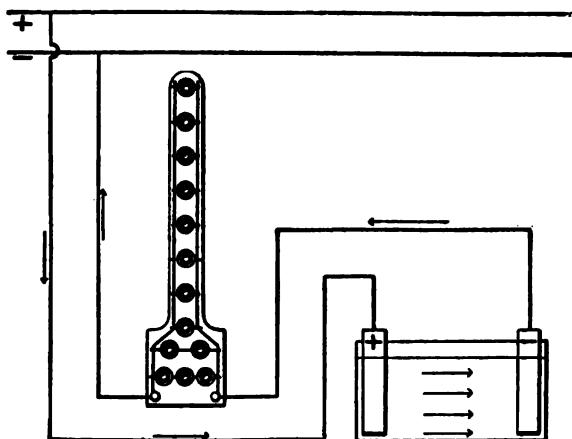
FIG. 6.—Diagram of Lamp-bank and Electrolytic Cell in Connection with a 110- or
a 220-volt Direct-current Electric-lighting Circuit.

This lamp-bank, which is the special design of the author, has proven
so useful in many electrochemical processes that an enlarged diagram
of it is given in Fig. 7.   When connected with the 110-volt circuit
a 16-candle-power lamp inserted in any of the single sockets A allows
about $\frac{1}{2}$ ampere to pass.   With all eight of the single sockets filled,
it allows about 4 amperes to flow; and if these same sockets are
filled with 32-candle-power lamps, a current of about 8 amperes
will be obtained.   Now, for a more feeble current, less than $\frac{1}{2}$ ampere,
two 16-candle-power lamps are placed in the sockets BB, and a
current flow of about $\frac{24}{100}$ will be obtained.   With three of these
lamps in the sockets CCC, a current of about $\frac{18}{100}$ will be allowed to
pass; 220-volt lamps may be used here in series, when the current
will be less than $\frac{1}{10}$ ampere.   This is only in accordance with the

well-known law of Ohm: $C = R \div V$, where C is the current, R the resistance, and V the voltage. A 32-candle-power 110-volt lamp has a resistance of about 110 ohms, a 16-candle-power lamp about 220 ohms, and a 220-volt lamp about 440 ohms. So it will be seen that with the three kinds of lamps at hand a very flexible lamp-bank results from the design given.
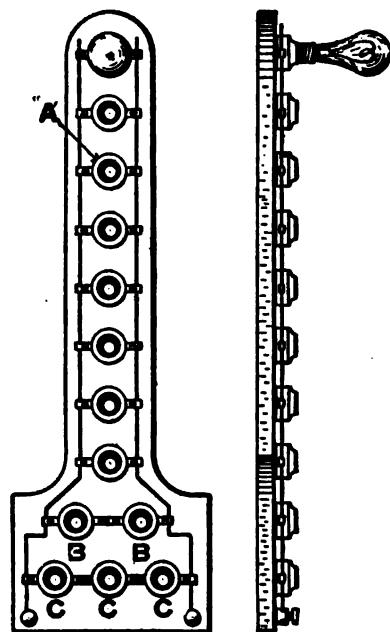
FIG. 7.—Laboratory Lamp-bank for Electrolytic Work. Range from $\frac{1}{100}$ ampere to 8 amperes.

However, for certain work the high potential of the electric-lighting circuit is not desired, and the lamp-bank, no matter how designed, will not meet requirements. Again, should we require 20 amperes of current for certain work, the lamp-bank would have to hold twenty 32-candle-power lamps, or forty 16-candle-power lamps, and would be very wasteful of energy when we consider that we are working under a difference of potential of at least 110 volts; 110 volts × 20 amperes would represent 2200 watts, which would be nearly 3 horse-power; 2200 watts divided by 746 (number of watts to the horse-power) equal 2.94 horse-power. Whereas we would require the 20 amperes for our electrolysis, we could not only get along with 4 volts pressure, but would actually prefer it, so we

use a motor-generator, and consume something like 80 watts, instead of the 2200. 20 amperes × 4 volts = 80 watts. The photograph, Fig. 8, shows a simple form of motor-generator used by the author
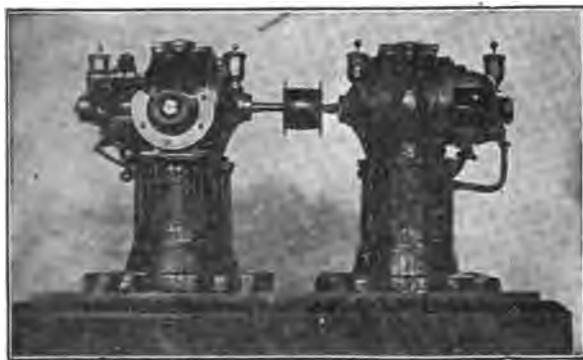
FIG. 8.—Photograph of a Motor-generator used to Convert the 110-volt Lighting Current into a 15-ampere Current at 4 Volts Pressure, which are the ideal conditions for many electrochemical processes for experimental purposes.
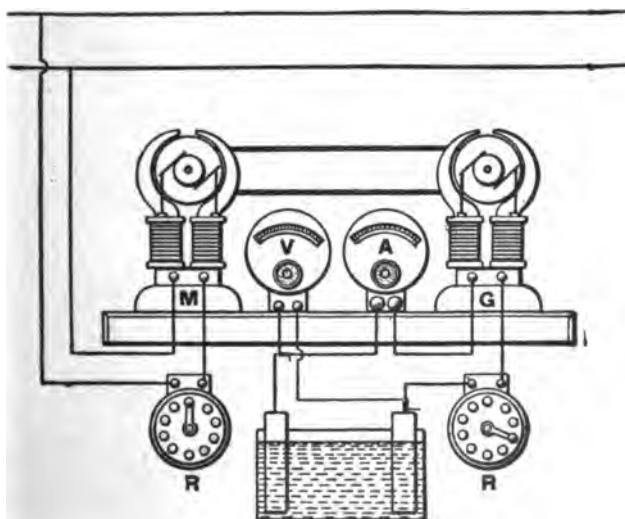
FIG. 9.—Diagram of Motor-generator and Electrolytic Cell in connection with Electrical Measuring-instruments for Observing Electrical Conditions within the Electrolyte. Here the comparatively high-voltage electric-lighting current is stepped down to the ideal voltage for electrolysis of chemical compounds.

for the past six or seven years, which gives about 20 amperes at a pressure of only 4 volts, the driving-motor taking a trifle more than the corresponding number of watts.

The last illustration in our present chapter is a diagram of a similar motor-generator, but of the belted type, and represents electrical measuring instruments properly connected for observing the watts used in the electrolyte for any kind of electrolytic work. Here M is the driving-motor, G the generator, V and A the voltmeter and ammeter respectively, and RR rheostats for controlling the speed of the motor on the one hand and the current supplied to the electrolytic cell on the other. The generator is of the shunt-wound type, and it is very necessary to have a good variable resistance in the outside circuit. The ammeter shows the current taken and the voltmeter the drop of potential across the electrodes. Such a small rotary converter can be ordered from almost any of the manufacturers of small dynamos and motors. Having outlined the simple apparatus necessary for practical work on a small scale, we will close the present chapter with definitions of the technical terms introduced and continue the development of the subject in the next chapter.

Electrolysis.—The breaking up of chemical compounds by the electric current, and the setting free at the electrodes of the constituents.

Electrode.—The terminal of the source of electricity which dips into the electrolyte.

Electrolyte.—A chemical compound, capable of conducting the electric current when in solution or in the fused state.

Anode.—The positive electrode in an electrolyte. The electrode from which the electric current flows.

Cathode.—The negative electrode in an electrolyte. The electrode to which the electric current flows.

Ion.—A chemical atom or group of atoms possessed of an electrical charge.

Electrolytic conductivity.—The passage of the electric current through an electrolyte accompanied by the movement of ponderable material. Ion transfer. The carrying of the electric current by moving ions.

Electrolytic dissociation.—The breaking up of certain chemical molecules when dissolved in water or other suitable solvents, into ultimate parts charged with electricity.

CHAPTER II.

THE THEORY OF ELECTROLYTIC DISSOCIATION.

In the last chapter, that beautiful doctrine known generally as the theory of electrolytic dissociation was touched upon, and the reader was asked to accept upon faith the truth of its meaning for the time being. It is the purpose of the present chapter to advance some of the best experimental evidence in its support, and leave the student to formulate his own opinions. Probably there is no generalization in the entire domain of physical chemistry quite so unique and attractive as the theory advanced as recently as 1887 by Svante Arrhenius, now professor at the University of Stockholm. Few theories in either chemical or physical science have been the subject of greater dissertation, dispute, or attack than the dissociation theory, and few have served a more useful purpose in accounting for certain vital phenomena. The theory of electrolytic dissociation has the most excellent experimental evidence in its favor, and accounts perfectly for many heretofore unexplained facts, and those urging objections to its truth have never been able to propose a better one, or even one half as good. It will be the effort of the present writer to advance what he considers to be the best and most forcible evidence for this doctrine, and adopt it throughout in the practical electrochemical studies which are to follow. Until something better is brought forward, we will not take our time in making attacks upon the doctrine. The arguments against the theory will not be introduced for fear of confusing the student. We know from previous experience that we have, broadly speaking, two kinds of conductors of the electric current—the metals and alloys on the one hand, and solutions of certain chemical substances on the other. In the case of the metals and alloys they are called conductors of the first class, and in the case of chemical substances in solution or in a state of fusion they are called conductors of the second class. The passage

of an electric current through a conductor of the second class is believed to be accompanied by the actual movement of ponderable material, or a mechanical transfer of matter. Good evidence in support of this will be introduced a little later.

We may now take all known chemical compounds and divide them into two great groups as follows: 1st. Those compounds which when dissolved in water or other suitable solvent conduct the electric current; 2d. Those compounds which when dissolved do not conduct the electric current. For this purpose we may draw a dividing line separating these two great classes, and term those which conduct when in solution, electrolytes, and all those which do not conduct the electric current when in solution, non-electrolytes. In the following table a few chemical compounds of both kinds are given. This table could, of course, be indefinitely extended, but a sufficient number of compounds are given to show the character and meaning of the division. Upon examining the bodies in the left-hand column it will be observed that all the electrolytes are among, and constitute,

CHEMICAL SUBSTANCES.

Electrolytes.		Non-electrolytes.	
Sodium chloride.	NaCl	Cane-sugar.	$C_{12}H_{22}O_{11}$
Sodium nitrate.	$NaNO_3$	Ethyl alcohol.	C_2H_5OH
Potassium sulphate.	K_2SO_4	Methyl alcohol.	CH_3OH
Ammonium hydroxide.	NH_4OH	Benzene.	C_6H_6
Sodium hydroxide.	NaOH	Chloroform.	$CHCl_3$
Potassium hydroxide.	KOH	Ether.	$(C_2H_5)_2OH$
Sulphuric acid.	H_2SO_4	Acetic aldehyde.	CH_3CHO
Nitric acid.	HNO_3	Formic aldehyde.	HCHO
Hydrochloric acid.	HCl	Acetone.	CH_3COCH_3
Acetic acid.	CH_3COOH	Propyl alcohol.	C_3H_7OH
Oxalic acid.	$C_2H_2O_4$	Amyl alcohol.	$C_5H_{11}OH$
Silver nitrate.	$AgNO_3$	Isopropyl alcohol.	C_3H_7OH

the "chemically active" bodies, whereas the non-electrolytes constitute the "chemically inactive" bodies. It will be observed that certain chemical substances are electrolytes only when dissolved in water or other suitable solvent, or when in the fused condition, according to the definition of an electrolyte. We may take any of the chemical compounds in the left-hand column, including even the acids, and when absolutely water-free they are non-conductors of the electric current. Water itself, when properly distilled and air-

free, is also a non-electrolyte (except to an infinitesimal extent), and yet when certain chemical substances are dissolved in water they become most excellent conductors of electricity.   See Fig. 10 for a simple experiment for distinguishing electrolytes from non-electrolytes. The lamp-bank and electric-lighting circuits, or the motor generator as described in the first chapter, may, of course, be used instead of the storage-battery as given here.   Here we may have the case where two bodies, when separated, each prove to be non-conductors, and when brought together, to conduct highly the electric current.   What is it due to?   To take a special case, a crystal of rock salt (sodium chloride) and carefully distilled water.   Neither of these substances will conduct the electric current to any appreciable extent.   Dissolve
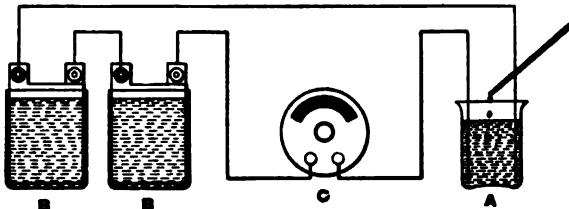
FIG. 10.—Simple Apparatus for Distinguishing Electrolytes from Non-electrolytes. *A*, glass beaker containing distilled water with platinum electrodes into which the compound to be tested is dropped; *C*, milli-amperemeter; *BB*, cells of storage-battery.   There is always a slight indication of conductivity upon a sensi.ive milli-amperemeter when only the glass beaker and distilled water are present, due to the dissolving of a minute trace of glass together with impurities in the distilled water.   The amount of deflection can be noted and applied as a correction.

the salt in the water and the solution has a high conductivity.   Something must have taken place within the water, and yet we know we have made only a simple solution of salt in water, which when evaporated to dryness, gives back our salt unaltered, and if we catch and condense the water driven off, we have ordinary distilled water again.   What is the condition of the salt in the water, then, to so greatly change its physical behavior toward the electric current?   In terms of the theory of electrolytic dissociation, as was pointed out in the previous chapter, the chemical molecule is broken up into "ions" or ultimate parts, and these ultimate parts bear electrical charges upon them.   The molecular formula of sodium chloride is represented simply thus, NaCl, so familiar to all general chemists.   Now upon immersion in water the molecule is believed to be broken up as

follows into two "ions," $\overset{+}{Na}$ and $\overset{-}{Cl}$, the bond or attraction between the two former atoms being broken, and the sodium ion with its electrical charge is existing independently of the chlorine ion with its electrical charge of unlike polarity or sign. The mere act of passing into solution is believed, in terms of our theory, to separate the atoms of certain molecules, the atoms becoming ions at once by taking upon themselves electrical charges of opposite signs, the one becoming a positive ion, the other a negative ion. In the previous chapter it was pointed out, by means of a diagram, that the positive ion traveled to the negative electrode, and that the negative ion traveled toward the positive electrode. It is the purpose of this chapter to show that we have excellent reasons for believing in the existence of these electrically charged particles when certain chemical substances are dissolved in water. We will take up the study of the evidence first by comparing the deportment of substances in aqueous solution with substances in the state of a gas, and for this purpose we will first set down the three gas laws so well known to all students of modern chemistry and physics.

Law of Boyle. The pressure exerted by a gas, the temperature remaining the same, is proportional to the concentration of the gas. The concentration of the gas is directly proportional to the number of molecules or ultimate parts of molecules present.

Law of Gay-Lussac. The pressure of a gas increases a constant amount for every increase of $1°$ in temperature, and the increase in pressure is equal to $\frac{1}{273}$ of the original pressure of the gas at $0°$ C.

Law of Avogadro. Equal volumes of all substances in the gaseous state, under the same conditions of temperature and pressure, contain the same number of molecules or ultimate parts of molecules.

Consequently the molecules of all substances, or the ultimate parts of all molecules when in the gaseous state, under the same conditions of temperature and pressure, *occupy the same space.*

Having the three fundamental gas laws before us, we will take them up separately in the order given, and learn what bearing they have upon the behavior of substances in solution. What possible application can these gas laws have to chemical compounds dissolved in water? There appears to the general student to be no connection whatever, and yet there is the most vital application of the gas laws in support of the theory of electrolytic dissociation. Let us first

take up Boyle's law, which has to do with the pressure exerted by substances in the state of a gas. This tells us facts based upon experimentally determining the pressures exerted by gases of different concentrations. The pressures of gases confined in given volumes at constant temperature can be readily measured by manometers or pressure-gauges, as set forth in detail in any good text-book on physics. This we know; but can we measure the pressures exerted by substances in solution? We can convert a given mass of a given substance into a gas by heating, and measure the pressure at different concentrations, or volumes, by means of suitable manometers. If we dissolve the same quantity of the compound in water, will the molecules exert a pressure in the dissolved condition, and can we measure it? Both these questions can be answered in the affirmative, and it is the purpose here to show that such pressures exist, and to describe how they may be measured. All substances when dissolved in water exert a pressure, and this pressure has been termed "osmotic pressure."

OSMOTIC PRESSURE AND METHOD OF MEASURING IT.

If a gas, oxygen or hydrogen for example, be liberated in a given space, the gas will expand in all directions and completely fill the containing vessel. If all parts of this containing vessel are at the same temperature, the gas will expand and distribute itself uniformly throughout the volume. There will be repellent forces between the molecules of the gas, driving them to the remotest recesses of the containing vessel, and consequently there will be a pressure against the walls of the same. The more concentrated the gas, or, in other words, the greater the number of molecules or ultimate parts of molecules present, the greater will be the pressure within the fixed or given volume. What can be said about substances in solution? The behavior is the same. Let us take a large vessel of water, for example a tall glass jar full, and introduce a little sugar in it. The sugar will immediately fall to the bottom, a small portion dissolving and passing into solution on the way down. What will be the ultimate result on standing? The sugar at the bottom will all pass into solution, rise against gravity, and in time distribute itself uniformly throughout the solvent. The sugar in the dissolved state will behave exactly as it would when in the state of a gas, and

will exert a pressure when in solution which may be measured. This is due to the phenomenon of diffusion, which, not so many years ago, was wholly unaccounted for. Here we have a heavy substance dissolving at the bottom of a tall glass cylinder filled with water, and rising to the top against the attraction of gravity. There is a pressure, and this pressure has only recently been accounted for. Another phenomenon which until recently could not be explained was the bursting of an animal bladder, filled with a mixture of alcohol and water, when immersed in a vessel containing pure water. The bladder under these conditions, if it has been closed up properly at the openings, will be burst by a gradually developed pressure within. It is easy to show in this way that we have a pressure, and this pressure has been termed osmotic pressure. This is only a very crude method of showing qualitatively that we have a positive pressure, and it does not seem to have occurred to the earliest workers that this pressure was a definite thing and could be quantitatively measured. This osmotic pressure is a very peculiar thing when one considers the manner in which the pressure is measured. We cannot place a solution within a closed vessel and get an indication of pressure upon a gauge-glass or manometer, as we very well know, but must resort to some kind of a membrane, such as forms the animal bladder. Strange to say, the pressure developed depends upon a differential, or selective action, so to speak, of the necessary membrane. It must allow the solvent to pass through, but not the dissolved substance, a sort of filter, roughly speaking, and because of this principle the membrane has been called "semipermeable." Now if we can really produce a semipermeable membrane or diaphragm, we will be able to measure the pressure due to substances in solution. Take, for example, a solution of cane-sugar. If we have at hand a membrane which will be permeable to water and impermeable to sugar, we can by its use ascertain the pressure due to the presence of the sugar molecules, and demonstrate how this pressure varies with concentration of the solution and with changes in temperature. We have at hand, in other words, means for comparing the behavior of gas molecules with the behavior of molecules in solution. Let us prepare such a semipermeable membrane in the laboratory and examine some of the compounds given in the preceding table constituting electrolytes on the one hand and non-electrolytes on the other.

The accompanying photograph illustrates some simple forms of porous pots, and Fig. 12 gives a section through such a typical pot, as well as a completed piece of apparatus for experimentally measuring osmotic pressure. Moritz Traube, and Pfeffer, the celebrated plant physiologist, were the first to discover and make use of the properties of semipermeable membranes. It is to Pfeffer that we owe the first really serviceable artificial semipermeable diaphragm or partition.

FIG. 11.—Some Forms of Porous Pots with Semipermeable Membranes for the Measurement of "Osmotic Pressure." The broken exhibit shows the semipermeable membrane at M.

It was discovered by Pfeffer that plant and animal membranes could be discarded, and that certain chemical precipitates, when properly supported, met the requirements almost perfectly. Copper ferrocyanide was found to give the most satisfactory results when formed right in the walls of a very fine-grained unglazed porous pot. In order to produce such a precipitate within the walls of the porous pot, it was filled with a solution of potassium ferrocyanide and immersed in a solution of copper sulphate. The two solutions met within the walls and there formed the semipermeable membrane with the resistant support of the porous pot. When such a prepared

pot is broken open, the membrane appears in the form of a fine line, as indicated in Fig. 11 at *M*. There are many necessary precautions to be taken in the preparation of successful semipermeable membranes, it being an art requiring not a little patience and skill. The following is taken from one of Pfeffer's writings on the subject: "The porcelain cells were first completely injected with water under the air-pump and then placed for at least some hours in a solution containing at least 3 per cent of copper sulphate, and the interior was also filled with this solution. The interior only of the porcelain cell was then rinsed out quickly with water, well dried as rapidly as possible by introducing strips of filter-paper, and after the outside had dried off, it was allowed to stand some time in the air until it just felt moist. Then a 3 per cent solution of potassium ferrocyanide was poured into the cell and this immediately reintroduced into the solution of copper sulphate. After the cell had stood undisturbed for from twenty-four to forty-eight hours, it was completely filled with the solution of potassium ferrocyanide and closed. . . . A certain excess of pressure of the contents of the cell now gradually manifested itself, since the solution of potassium ferrocyanide had a greater osmotic pressure than the solution of copper sulphate. After another twenty-four to forty-eight hours the apparatus was again opened and generally a solution introduced which contained 3 per cent of potassium ferrocyanide and 1½ per cent of potassium nirate (by weight), and which showed an excess of osmotic pressure of somewhat more than three atmospheres."

In all this work as reproduced by the present writer is was found most essential to obtain a special close-grained grade of porous cup or pot. A common porous pot, or one the least faulty, such as containing minute invisible fissures, will defeat the object of the entire experiment. With faulty pots the writer has frequently had a completed piece of apparatus assembled, indicating a height of only 2 or 3 feet of the contained solution, when the semipermeable membrane gave way and oozed through the side of the porous pot. It has been found that a dilute solution of cane-sugar in water would rise to a height of 66 feet. Referring once more to Fig. 12, we will note a rise of about 2 feet, a one-half normal sugar solution being used in this case. Strange as it may seem, the sugar solution is placed within the porous pot *A* and the pot is in turn immersed in the beaker *B*,

containing distilled water. The pressure is developed within the
porous pot by a very curious action, forcing the liquid up into the
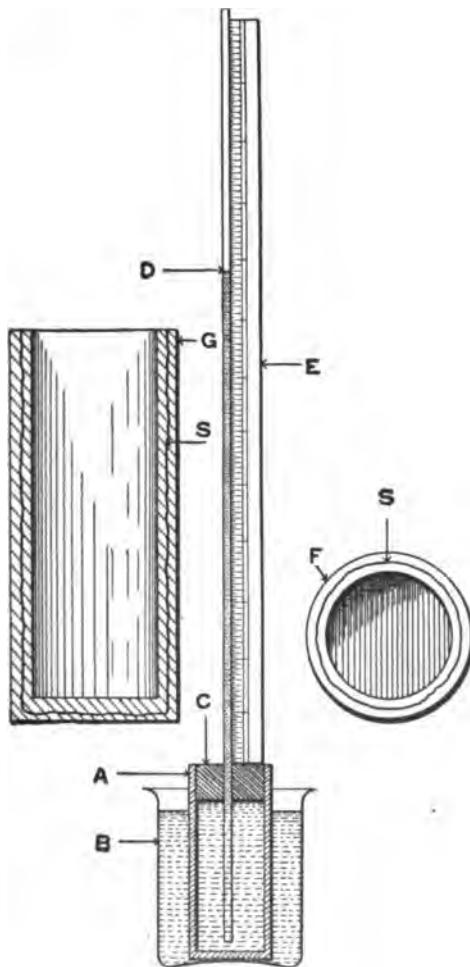
FIG. 12.—*A*, porous pot; *B*, glass beaker; *C*, tight-fitting stopper; *D*, height to
which the contained solution has risen; *E*, graduated scale; *F*, transverse sec-
tion of porous pot; *S*, semipermeable membrane within the wall of the pot;
G, enlarged vertical section through porous pot with semipermeable membrane
showing at *S*.

manometer-tube. The conditions are as follows: The semiper-
meable membrane allows water to pass through freely, but does
not allow the sugar molecules to pass. Within we have sugar

molecules and water molecules attempting to get out, and outside we have all water molecules attempting to get in. Now, we have, per unit area of the porous pot and semipermeable membrane, a more effective bombardment from the pure-water molecules without than from the mixed molecules within. We may think about the thing also as follows: Every water molecule striking the diaphragm from the outside gets in, but many of the water molecules before striking the diaphragm from the inside collide with sugar molecules, which cannot get through, and thereby their effectiveness is lost. As a result of such a differential action we may have a slow ingress of water molecules tending to dilute the sugar by driving its molecules farther apart and thereby establishing a pressure. Let us leave the theory of the apparatus now and look at the facts in some actual and carefully conducted experiments.

OSMOTIC PRESSURE OF NON-ELECTROLYTES AND ELECTROLYTES.

For the sake of simplicity we will record the result of an osmotic-pressure determination upon a non-electrolyte. For this purpose we will choose the first non-electrolyte appearing at the top of the column in the little table already given. This is ordinary cane-sugar, a solution of which in water does not conduct the electric current. The following table shows the result of one of Pfeffer's carefully conducted determinations upon this substance:

CANE-SUGAR, $C_{12}H_{22}O_{11}$.

Concentration in Per Cent by Weight.	Osmotic Pressure in Millimeters of Mercury.
1	535
2	1016
4	2082
6	3075

Let us now examine the figures standing for osmotic pressures and interpret their meaning.

Concentration, C.	Pressure, P.	$\dfrac{P.}{C.}$
1 per cent	535	535
2 " "	1016	508
4 " "	2082	521
6 " "	3075	513

In the above table the pressure in each case has been divided by the concentration with practically a constant resulting. What little

discrepancy exists is due to experimental error. Here we have an analogy with the law of Boyle as applied to gases. We know that the pressure of a gas increases with its concentration in a direct proportion, and we see from the above tabulated data that the osmotic pressure of a solution increases directly with its concentration. In experimental work of this character there are naturally sources of error which must be expected. For example, when we start with a 1 per cent sugar solution and begin to measure its osmotic pressure by such a piece of apparatus as described, the solution is weakened by the inflow of water, and unless the manometer-tube is very small, the volume of sugar solution rising to make the indication will constitute a high percentage of the entire volume in the porous cup. Pfeffer also showed, at the instigation of Van't Hoff, that the osmotic pressure of solutions increases slowly with rise in temperature, and that this pressure is analogous to the increasing pressure of a gas as set forth in the law of Gay-Lussac. Here a solution of sugar was taken again, but instead of varying its percentage strength the temperature of the solution was gradually increased. For this purpose a one-tenth normal sugar solution was employed (a normal solution of cane-sugar is made by dissolving a gram-molecular weight of this compound in a liter of water. A one-tenth normal solution is made by dissolving the gram-molecular weight in 10 liters of water), gradually increasing its temperature. The accompanying table shows the data of an actual experiment.

Temperature.	Osmotic Pressure in Cm. of Mercury.	
	Experimental.	Calculated from Gas Law of Gay-Lussac.
6.8°	50.5	50.5
13.5°	52.1	51.7
14.2°	53.1	51.8
22.0°	54.8	53.2

While there are slight discrepancies due to experimental error, the striking application of Gay-Lussac's law to substances in solution is to be noted. Although Pfeffer was the first to successfully measure osmotic pressures, it remained for Van't Hoff to bring out the striking agreements with the gas laws already set forth. Having

observed the strong tendency of solutions to behave like substances in the state of a gas, by experimenting with semipermeable membranes this great Dutch scientist investigated other possibilities for showing analogies, among them being what is known in physical chemistry as the "Principle of Soret."

The Principle of Soret.

If a vertical glass tube is filled with a solution of a chemical compound, such as copper sulphate in water, for example, and the two ends of the tube are kept at different temperatures, the copper sulphate will eventually become more dilute where the temperature is highest and more dense where the temperature is lowest. This distribution of the dissolved molecules by diffusion due to differences in temperature is known as the principle of Soret. The apparatus shown in Fig. 13 is the design of the present writer for bringing about such concentration changes. The tubes filled with various solutions were allowed to stand for a long time with the top and bottom at different temperatures, when some of the solution was allowed to run out from the bottom and analyzed for density, and some of the solution drawn out from the top by means of a pipette and also analyzed for density. The early experiments showed smaller differences in concentration than would be called for if Gay-Lussac's law applied to the temperature coefficient of the osmotic pressure of solutions. The tubes were then allowed to stand for longer periods of time, with the result that the figures obtained approached closer and closer to the value expected from the law pertaining to gases. Diffusion of molecules takes place very slowly and the tubes had to stand for many weeks undisturbed before an equilibrium was finally established. In one experiment where the tubes stood for about twelve weeks a copper-sulphate solution gave the following results:

Upper end of tube 80° C.; lower end of tube 20° C. The difference in density between the respective ends of the tube upon analysis was found to be 14.03 per cent. The difference in density calculated from the law of Gay-Lussac is 14.3 per cent. Another experiment gave 24.87 per cent change in concentration when according to Gay-Lussac's law the figure should have been 24.8 per cent.

Here the application of Gay-Lussac's law to the behavior of compounds in solution is very striking. With the apparatus as
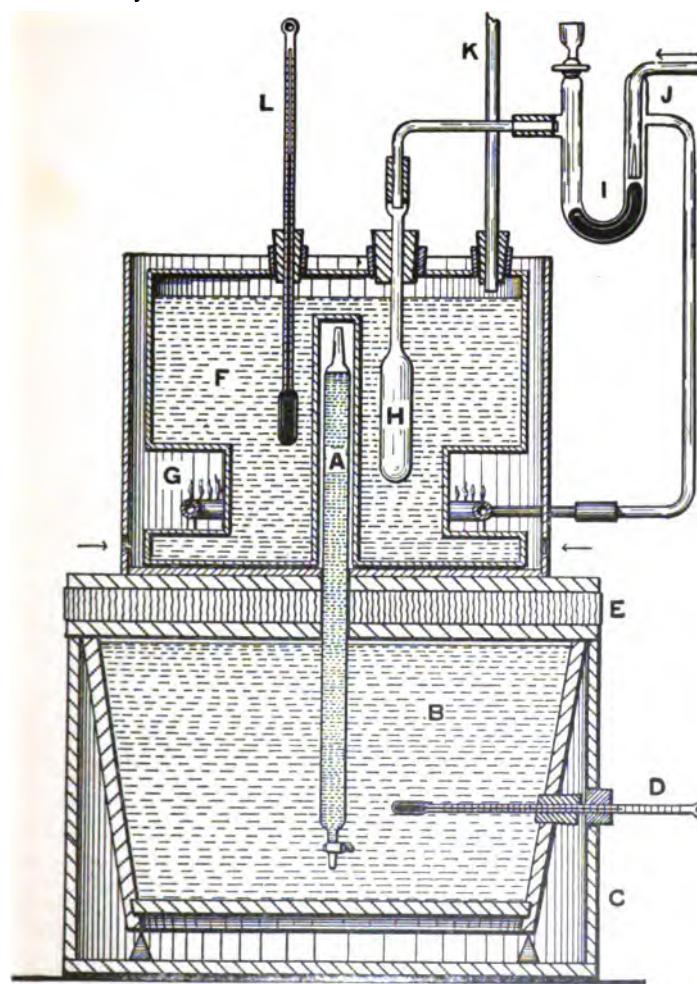
FIG. 13.—The "Principle of Soret" (Author's Apparatus). *A*, vertical glass tube containing the substance; *B*, water in wooden tub; *C*, outer wood casing to be filled in between with charcoal or sawdust; *D*, thermometer; *E*, heavy layer of hairfelt between thick boards supporting top of apparatus; *F*, water in copper heater; *G*, ring gas-burner for heating water; *H*, bulb of air-thermostat for holding temperature of water constant; *I*, mercury of air-thermostat for cutting off gas-supply, *J*, if the temperature rises too high; *K*, long vertical glass condensing-tube to prevent loss of water, *F*, by distillation; *L*, thermometer for observing temperature.

illustrated, the large mass of water in the wooden tub, together with a laboratory kept at practically constant temperature, the lower end of the tube is consequently very uniformly maintained in temperature. The upper end of the tube is kept at an elevated temperature by means of the ring gas-burner and the sensitive air-bulb thermostat. The expansion of the air contained in the air-bulb H forces the mercury at I up to the tube J which is slotted, and gradually cuts off the supply of gas which enters as indicated by the small arrow. Should the temperature of the water F fall below the required temperature, the air in the bulb H will contract and allow the mercury to fall away from the tube J, thus uncovering the slot and allowing more gas to flow to the burner. Two very sensitive thermometers give the readings for the top and bottom of the tube respectively. The apparatus is so designed that the top portion may be lifted off, when the tube containing the solution experimented upon may be readily removed. It remains now to compare the behavior of substances in solution with the third and last gas law, namely, that of Avogadro. This was also done by the chemist Van't Hoff. He worked again with a solution of cane-sugar, and compared the osmotic pressure of such a solution with a volume of hydrogen gas of equal concentration. For this purpose he made a cane-sugar solution having the same number of sugar molecules in a given volume of solution as there are hydrogen molecules in the same volume of the gas. The experiment fully justified the statement that the sugar solution gave an osmotic pressure equal to the gas pressure. *We may then say that equal volumes of all chemical compounds in solution giving the same osmotic pressure at the same temperature contain the same number of molecules or ultimate parts of molecules.* Now this is only true for di ute solutions. Very concentrated solutions of chemical substances do not obey the law, and when we look about we are struck by the fact that very densely compressed gases do not obey the law of Boyle. This makes our comparisons all the more striking, for where we have exceptions in the case of gases, we also have exceptions in the case of solutions. It has now been shown that the three fundamental gas laws apply to compounds in a state of solution, but what has this, although striking and of vital interest to the physical chemist, to do with the theory of electrolytic dissociation? To answer this let us turn once more to the first table of this chapter where we have

electrolytes on the one hand and non-electrolytes on the other. It was pointed out that all those bodies have been classified according to their ability to conduct the electric current. All those on the left conduct when in solution, and all those on the right do not. All those on the left are called electrolytes, and in terms of the theory of electrolytic dissociation, their molec les break up into ions, each ion of course being an ultimate part of a molecule. Now as a matter of fact, only the non-electrolytes,· when dissolved in water, obey the gas laws. It is only the non-electrolytes which give an osmotic pressure comparable with substances in the state of a gas, the electrolytes all giving an abnormally high osmotic pressure. This is just what we would expect if one molecule breaks up into two ultimate parts and each ultimate part occupies the same space as the original molecule. Our sugar molecule does not conduct the electric current when in solution, it does not break up into ions, and gives as evidence a normal osmotic pressure. Our sodium chloride, or common salt, does conduct the electric current when dissolved, and it gives an abnormally high osmotic pressure. Of course in comparing the osmotic pressure of sugar with sodium chloride, two solutions are made in which the same number of molecules are dissolved in each case. In order to accomplish this the gram-molecular weight of each compound is taken. By gram-molecular weight of a compound we mean the molecular weight of the substance expressed in grams. For example, the gram-molecular weight of sodium chloride is 58.5 grams, 58.5 being the molecular weight of sodium chloride. So much for the theory of electrolytic dissociation and the gas laws and the evidence that the measurement of osmotic pressure gives us in favor of ionization. We will take up additional evidence in support of the theory of electrolytic dissociation in our next chapter.

CHAPTER III.

It is well known that pure water freezes constantly at 0° C., and that this fact has been made the basis for the several thermometric scales for scientific purposes throughout the world. It has also been well known from very early times that the addition of salts or other soluble material to water causes it to freeze at a lower temperature. Every schoolboy knows that common sea-water will not freeze except at very low temperatures, but few of us who have not paid attention to physical chemistry have given the fact more than a passing thought. We know that substances in solution cause pure water to freeze at a lower temperature than pure water alone; in other words, that the freezing-point is lowered by the presence of dissolved substances. This is purely qualitative knowledge, so to speak, and there remains for us to investigate this matter quantitatively, to see how much solutions of the same concentration lower the freezing-point, and if all compounds lower it equally. Raoult, the celebrated French chemist, took up this matter for experimental investigation, and, to make a long story short, found that all non-electrolytes of equal concentration lowered the freezing-point of pure water to the same extent. Raoult worked with solutions containing one gram-molecule of the dissolved substance per liter and found that the lowering of the freezing-point was the same, being 1.85° C. One gram-molecule of a substance per liter is a normal solution, and we may say therefore that all normal solutions of non-electrolytes lower the freezing-point of water 1.86° C. This is comparable to saying that the lowering of the freezing-point of pure water is dependent upon the number of molecules or ultimate parts of molecules present. This is, of course, an interesting fact, but what has it to do with the theory of electrolytic dissociation? This question can be very quickly answered by determining the lowering

of the freezing-point by normal solutions of electrolytes. What would we expect if the theory of electrolytic dissociation be true? Will a gram-molecule of an electrolyte dissolved in a liter of water give us the same depression of the freezing-point, namely, 1.86 C.? This was done by Raoult, and it was found that *in every case of an electrolyte the depression of the freezing-point was greater than 1.86° C.* It will be remembered that all electrolytes exerted a greater osmotic pressure than non-electrolytes, and now we see that all electrolytes lower the freezing-point to a greater extent than non-electrolytes. We can only account for these striking phenomena by attributing the abnormal behavior of electrolytes to the breaking up of the molecules, upon dissolving, into ions. The practical student, upon reading the work done by Raoult and noting his constant of 1.86° C., will want to know how much greater the depression of the freezing-point was found to be in the case of electrolytes, and what kind of a thermometer was employed when dealing with such small differences in temperature. The average electrolyte, when dissolved in water, depresses the freezing-point about twice as much as any non-electrolyte. As for the thermometer, it is far from the ordinary pattern, and is used in a special piece of apparatus. The best and most universally used apparatus is that of Beckmann, and is illustrated in one of its forms in Fig. 14. The thermometer in this particular case is simply one of great sensitiveness and refinement, reading direct to hundredths of a degree. Because of an exceptionally large bulb, the degree divisions are very long, allowing of very fine sub-division. With such a thermometer one-tenth of 1° C. is a large amount. The accompanying illustration should make the scheme of the apparatus clear, and it will be seen that it is a simple one to get up in the laboratory for actual work, the thermometer being the only costly element. For exceedingly accurate research work thermometers may be had reading to thousandths of a degree. There are also metallic thermometers with which temperatures are measured by the change in electrical resistance of a little coil of platinum wire, and the delicacy is almost without limit. For all practical purposes, however, a mercury thermometer reading to hundredths meets every requirement. The practical carrying out of an experiment with such a Beckmann apparatus as shown in Fig. 14 is as follows: An accurately weighed quantity of pure distilled water is introduced

in the tube *A*, which in turn is placed in the tube *B* and packed around with a mixture of ice and salt.   The large tube *B* provides an air-space around the tube *A*, and causes a more uniform freezing
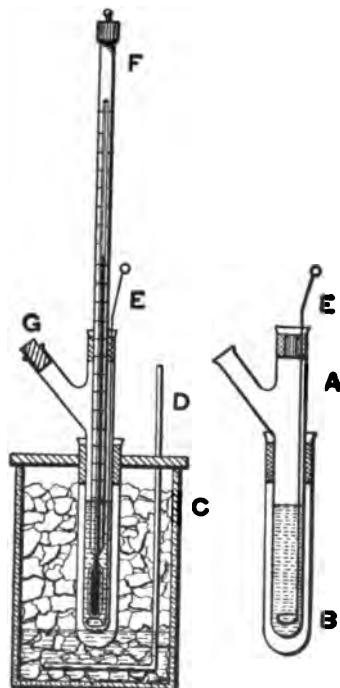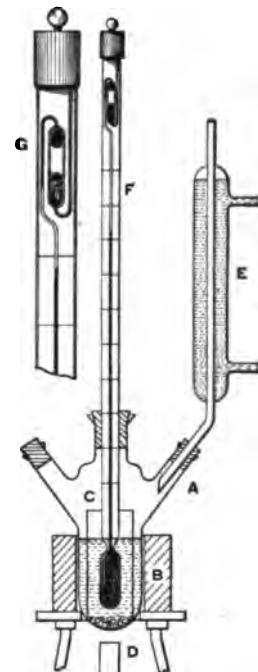
FIG. 14.   FIG. 15.

FIG. 14.—Form of Beckmann's Apparatus for the Study of Electrolytes and Non-electrolytes by Depression of Freezing-points. *A*, large glass test-tube with side neck; *B*, larger glass tube with cork to receive test-tube; *C*, large glass jar to receive both tubes and freezing-mixture; *D*, stirrer; *EE*, wire stirrers within test-tube; *G*, side neck into which the substance to be tested is placed; *F*, delicate "open-scale" thermometer.

FIG. 15.—Apparatus for Experimentally Determining the Elevation of Boiling-points of Electrolytes and Non-electrolytes. *A*, flask with double side necks; *B*, asbestos ring supporting flask on tripod; *C*, little cylinder of platinum within flask to prevent cooled condensed water from striking the thermometer-bulb; *D*, Bunsen burner; *E*, condenser with water-jacket; *F*, Beckmann thermometer with mercury-reservoir at top; *G*, enlarged view of mercury reservoir.

of the water in the inner tube.   The air between the two tubes becomes chilled below the freezing-point of pure water and freezes the water in the inner tube.   The stirrer *E* is moved up and down in the dis-

tilled water, and the thermometer is carefully watched. The mercury will fall steadily until the sudden formation of flakes of ice throughout the water occur, when it will quickly rise a little and remain stationary, and this reading should at once be taken. With a correct thermometer, the indication should of course be o° C. If the reading is not exactly o° it matters not, so long as we are merely measuring the differences between the freezing-point of pure water and water containing compounds in solution. At least three readings should be made with the same water, allowing the ice to melt and then freezing over again, and taking the average of the three temperatures for the freezing-point of the pure solvent. The sudden rise of the thermometer is due to a small supercooling of the water (in spite of the fact of its being stirred), below its freezing-point, and then its warming up again at the instant of the formation of ice It is well known to those who have studied physics that water throws off heat when it freezes, the phenomenon being attributed to latent heat. Having determined carefully the experimental freezing-point of the water, a carefully weighed quantity of the substances to be tested is introduced through the side tube D and allowed to dissolve. The freezing process is then repeated three times, as with pure water, and the average of the three readings is taken. If the water and compound have been so weighed as to give a normal solution, and the compound is a non-electrolyte, we will obtain the figure 1.86°, working, of course, with a centigrade thermometer. The important point to observe in making all these freezing-point determinations is to read the thermometer at once after the sudden rise of the thermometer, at the time of the formation of the ice. If we wait, and keep on with the freezing process, the thermometer will fall again, due to the fact that the solution has become concentrated by the freezing out of some of the water. This, of course, concentrates the solution and gives it a new and lower freezing-point. Electrolytes are treated in the same manner as non-electrolytes. There is another method which we should not pass over without notice, and that is the testing of electrolytes and non-electrolytes by the elevation of the boiling-point. It is well known that pure water boils at a constant temperature under a constant atmospheric pressure, and that the heights of mountains have been measured by the decrease in boiling-point of water with a delicate thermometer. It is also very well known

that the presence of dissolved substances increases the boiling-point of pure water. Raoult also investigated this phenomenon experimentally, and found that normal solutions of non-electrolytes increased the temperature of the boiling-point to the same extent. He also showed that all electrolytes of comparable concentration elevated the boiling-point to a much greater extent. Fig. 15 illustrates a piece of apparatus for experimentally determining the elevation of boiling-points with great accuracy. This special type of thermometer has an arbitrary scale, that is, it is not designed to indicate absolute temperatures, but only differences between temperatures. The little reservoir at the top contains a supply of mercury, which may be shaken down to join on to the column within the bore, thus allowing the instrument to be used with liquids of lower boiling-points. There are only about eight degree divisions upon the entire scale of such a delicate instrument, and were it not for the flexible character due to the mercury-reservoir, the use of such a thermometer would be exceedingly limited. With a set of two such instruments, one designed for low temperatures and the other for high temperatures, in view of the little reservoirs, we are equipped for experimental work throughout a very wide range. With either thermometer we may take from the reservoir, or return to the reservoir, by shaking the instrument, thereby making it serviceable for use at almost any temperature. In conducting experiments with this apparatus, a few fragments of broken glass are introduced in the flask to prevent "bumping" when the solution boils. We see, therefore, from these two experimental investigations of Raoult, that we have the most excellent evidence in favor of the theory of electrolytic dissociation.

ADDITIONAL EVIDENCE. THE NEUTRALIZATION OF ACIDS AND BASES.

One of the commonest and most familiar chemical reactions is the neutralization of an acid by a base with the formation of a salt and water. The following is a simple example, where hydrochloric acid and sodium hydroxide are brought together in solution:

$$HCl + NaOH = NaCl + H_2O.$$
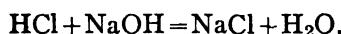
Here we have sodium chloride (common salt) and water formed in the reaction. So much for the general chemistry of the reaction. We also have a physical side to the reaction, and this concerns the

heat produced when the reaction takes place.   The general chemist
has to do with the products formed, and the physical chemist has
to do with the energy transformations and their measurement.
Now in the above reaction heat is liberated, and it remains for us.
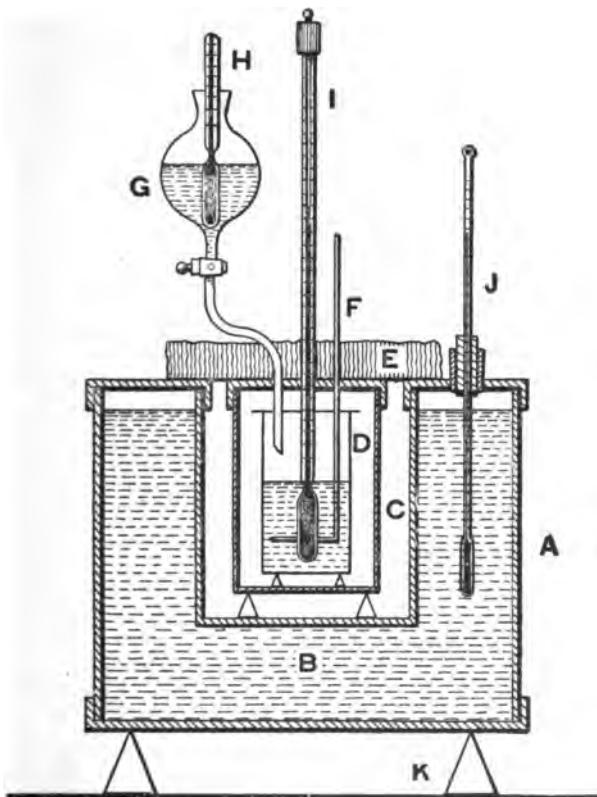
FIG. 16.—Calorimeter for Measuring the Heat Liberated when Solutions of Electro-
lytes are Mixed together and Allowed to React.   A, brass calorimeter-casing con-
taining mass of water, B.   There is also an inner calorimeter-casing of polished
metal, C, and the reaction-chamber, D; E, hair-felt covering; F, stirrer; G,
glass reservoir with stopcock; H and I, two similar thermometers of sensitive
type reading to hundredths of a degree; J, thermometer indicating temperature
of water-jacket; K, wooden wedges to insulate calorimeter.

to determine how much, and see if it has anything to do with our
theory of electrolytic dissociation.   Let us carry on such a chem-
ical reaction and experimentally measure the amount of heat given
out.   For this purpose we shall require a calorimeter like that
represented in Fig. 16.   It is easily made of polished brass by any

good sheet-metal worker, and is a valuable piece of apparatus for the physical-chemical laboratory. The inner reaction-chamber D should be of thin platinum, however. For our experiment we will place a normal solution of sodium hydroxide within the platinum chamber, and a normal solution of hydrocholoric acid within the glass reservoir with the stopcock turned off. The two thermometers are inserted, and the entire apparatus is allowed to stand for a sufficiently long time to allow equilibrium to be established. The thermometers are then read, and the hydrochloric acid from the reservoir is allowed to run into the calorimeter while the stirrer F is operated. The thermometer I is carefully watched until the mercury rises to the highest point. Now we are to measure the heat of the reaction in calories, and in order to do this it is only necessary to know the mass of the liquid raised through the indicated temperature, and to make the usual calorimetric corrections. We must know and allow for the specific heat of the mixture, the weight and specific heat of the platinum vessel, the heat exchange of the calorimeter, etc. The detailed method of working with calorimeters can be found in any good laboratory treatise on general physics. As a result of such an experiment with hydrochloric acid and sodium hydroxide we get 13,700 calories, in addition to the formation of the salt and the water. Now to come to the point; it matters not what acid and what base we use, or what salt is formed, we always get experimentally in such a calorimeter determination 13,700 calories. The following table indicates the run of things, and it now remains for us to interpret the meaning and see what it has to do with electrolytic dissociation. The first table gives a varying acid and a constant base, and the second table a varying base and a constant acid.

$HCl + NaOH$ liberates 13,700 calories.
$HBr + NaOH$ liberates 13,700 calories.
$HI + NaOH$ liberates 13,700 calories.
$HNO_3 + NaOH$ liberates 13,700 calories.

$HCl + LiOH$ liberates 13,700 calories.
$HCl + KOH$ liberates 13,700 calories.
$HCl + Ba(OH)_2$ liberates 13,800 calories.
$HCl + Ca(OH)_2$ liberates 13,900 calories.

In the case of the calcium and barium hydroxides, one-half normal solutions were taken to normal solutions of hydrochloric acid, for the reason that calcium and barium are bivalent. The above tables exhibit to us a remarkable performance, and it remains for the physical chemist to explain it. The theory of electrolytic dissociation explains it perfectly, and in so doing gains important experimental evidence in its own support.

$$\text{HCl and NaOH react and give NaCl and } H_2O.$$

In terms of our theory, however, these bodies would be dissociated and represented thus:

$$\overset{+}{H}\ \overset{-}{Cl} \text{ and } \overset{+}{Na}\ \overset{-}{OH} \text{ react and give } \overset{+}{Na}\ \overset{-}{Cl} \text{ and } H_2O.$$

Salt and water are the products, of course, but as the salt is born in water, so to speak, it is dissociated as represented as $\overset{+}{Na}\ \overset{-}{Cl}$, and not as NaCl, as it would be out of solution. The only thing really formed in the molecular state is water, and the constant of 13,700 calories is merely the heat of formation of water. All bodies have either a positive or a negative heat of formation, and if the salt is formed in the molecular condition along with the water, it would, of course, add its own heat of formation to the sum total, and as different salts have different heats of formation, we would, of course, not get a constant, but a different number of calories for each reaction between an acid and a base. The following table gives the heats of formation of a number of salts produced by the acids and bases which we have tabulated:

NaCl.	9,760 calories.
NaBr.	8,580 calories.
NaI.	6,910 calories.
NaNO$_3$.	11,130 calories.
LiCl.	9,380 calories.
KCl.	10,430 calories.
BaCl$_2$.	19,470 calories.
CaCl$_2$.	16,980 calories.

In the case of the calcium and barium chlorides, one-half the indicated number of calories must be taken, for the reason that cal-

cium and barium are bivalent and require double the quantity of acid.

It will thus be seen that without the theory of electrolytic dissociation we would be unable to explain the liberation of a constant number of calories, when an acid reacts with a base.

ADDITIONAL EVIDENCE.

Let us take four electrolytes, for example, and make two mixtures. For this purpose we will choose:

First mixture: Potassium nitrate, KNO_3;
              Sodium iodide, NaI.

Second mixture: Potassium iodide, KI;
              Sodium nitrate, $NaNO_3$.

Dilute solutions of both salts in each mixture are represented as follows, with all the constituents dissociated:

$$\overset{+}{K}\ \overset{-}{NO_3} \text{ and } \overset{+}{Na}\ \overset{-}{I};$$
$$\overset{+}{K}\ \overset{-}{I} \text{ and } \overset{+}{Na}\ \overset{-}{NO_3}.$$
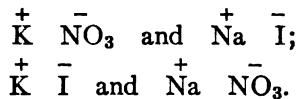
In terms of the theory of electrolytic dissociation we have exactly the same ions present in both cases, and the properties of the two mixtures should be absolutely the same. The two solutions, when equivalent quantities of the different substances are taken, are found to be identical in every respect.

FURTHER EVIDENCE. EXPERIMENTS WITH PERFECTLY DRY COMPOUNDS.

Let us take any of the "chemically active" bodies, or electrolytes, and inquire into their behavior when perfectly dry. In terms of the theory of electrolytic dissociation, dry electrolytes are in the molecular condition and are also "chemically inactive." In terms of the theory, the dissociation products, or ions alone, are capable of entering into chemical combinations. Let us test this matter carefully by referring to a number of experiments involving the careful drying of the substances employed. It is well known to

chemistry that ammonia gas, NH_3, and hydrochloric-acid gas, HCl, react at once to form ammonium chloride, NH_4Cl:

$$NH_3 + HCl = NH_4Cl.$$

The white clouds of ammonium chloride are even manifested when an ammonia bottle is unstoppered in the neighborhood of hydrochloric acid. It has been shown by the most careful and patient workers that thoroughly dry ammonia gas and thoroughly dry hydrochloric-acid gas do not react to form ammonium chloride, and may be separated after mixing in a thoroughly dry receiver. The accompanying illustrations show how this may be accomplished after the gases have been produced and thoroughly dried. The absolute drying of these gases is a difficult and tedious process,
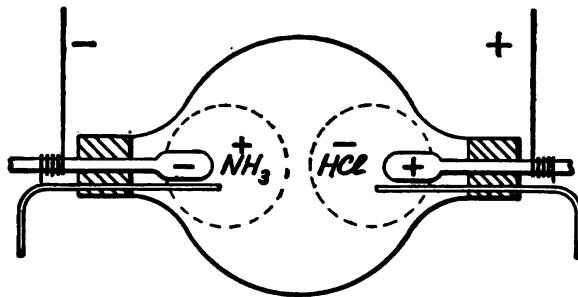
FIG. 17.—Diagram Representing an Uncombined Mixture of Dry Ammonia Gas and Dry Hydrochloric Acid Gas. The respective gases are here being separated by charged electrodes, where they may be drawn off and tested.

for the slightest trace of moisture in either the gases or the glass globe will defeat the object of the experiment.   They may, of course, be dried by passing through towers of finely broken lime and phosphorous pentoxide.   The globe must be heated to a high temperature by means of a Bunsen flame, while thoroughly dried air is passed through.   In every detail the most elaborate precautions must be taken against having moisture present.   In this case we have two molecules, NH_3 and HCl, behaving like ions, that is, the one goes to the positive pole and the other to the negative pole. The student may ask how it is that we have hydrogen going to the positive pole, as in the HCl diagrammatically represented within the globe in Fig. 17.   If he will turn to the first chapter and examine the elements arranged in their "electrochemical order,"

he will note that chlorine is much more strongly electronegative than hydrogen is electropositive, and being linked to the hydrogen, draws it to the positive pole. In the case of ammonia, we may think of the hydrogen winning and dragging the nitrogen to the negative pole, because there are three hydrogen atoms to the one
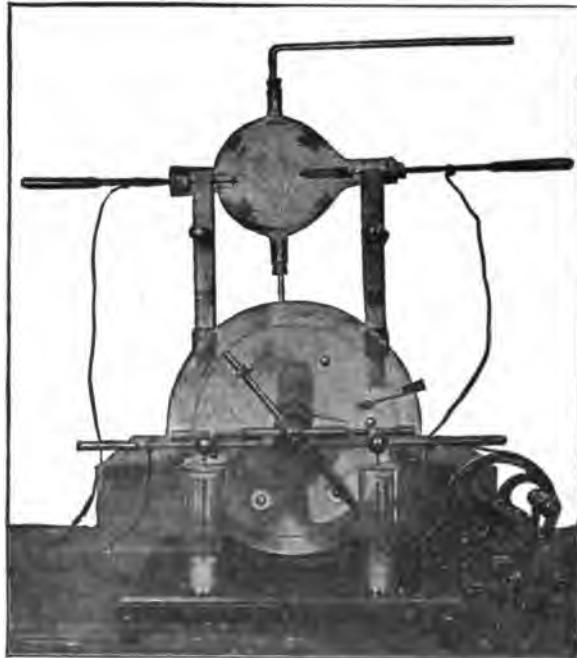
FIG. 18.—Glass Globe with Electrodes Leading to Static Machine for Separating a Perfectly Dry Mixture of Ammonia and Hydrochloric Acid Gases. After mixing together in the globe the gases may be separated by static charges upon the electrodes and be drawn off through the glass tubes.

of nitrogen in the ammonia molecule. Atom for atom nitrogen is more strongly electronegative than hydrogen is electropositive, as can be readily seen from the table, but there are three hydrogen atoms pulling the one nitrogen atom, and we may compare matters to a game of football where three players for one goal get hold of a single player for the other goal. The single player is pulling harder than any one of the others to make his goal because he is stronger, but he is overpowered in number. Fig. 18 shows a glass globe on an electrical machine for carrying out such an experiment.

So much for this experiment. The following list represents work done by various experimenters in support of the dissociation theory:

Perfectly dry sulphuric acid has been shown not to act on perfectly dry metallic sodium!

Dry hydrocholric acid does not act on carbonates.

Dry hydrogen and chlorine may be mixed together and exposed to the sunlight without an explosion taking place.

Dry hydrochloric-acid gas does not precipitate silver nitrate from water-free ether or benzene solution.

Dry acids will not act upon litmus paper, and will not form salts with dry bases.

Absolutely dry oxygen gas will not support combustion in many moisture-free substances!

Dry chlorine does not combine with metals, not excepting sodium and potassium.

Absolutely dry gunpowder could not be ignited!!

Allow the slightest trace of water vapor to enter the field in any of the above cases and we have immediate reactions. What part does the water play? In terms of our theory it is the dissociant, or cause for breaking down the molecules. Fig. 19 represents a molecule consisting of th atoms A and B, with the "chemical affinity" between them assigned to electrical attraction of unlike charges. The atoms in the molecule here are believed to be held together by electrical attraction. Now bring such a molecule into the presence of water. The negative atom will induce a positive charge in the water, and the positive atom will induce a negative charge in the water. Now, according to J. J. Thomson, one of England's most distinguished and famous physicists, because of these induced charges the attraction between the atoms A and B will be weakened, and when immersed in the water will be lost altogether. The following are Prof. Thomson's words describing the condition when such a molecule as represented in AB in the little diagram Fig. 20 is brought near a conducting sphere: "Thus let AB represent two atoms in a molecule, placed near a conducting sphere, then the effect of the electricity induced on the sphere by A will be represented by an opposite charge A', the image of A in the sphere. If A is very near the surface of the sphere, then the negative charge at A' will be very nearly equal to that of A. Thus

the effect of the sphere will be practically to neutralize the effects of A; as one of these effects is to hold the atom B in combination, the affinity between the atoms A and B will be almost annulled by the presence of the sphere. Molecules condensed on the surface of the sphere will thus be practically dissociated. The same effect would be produced if the molecules were surrounded by a substance possessing a very large specific inductive capacity. Since water
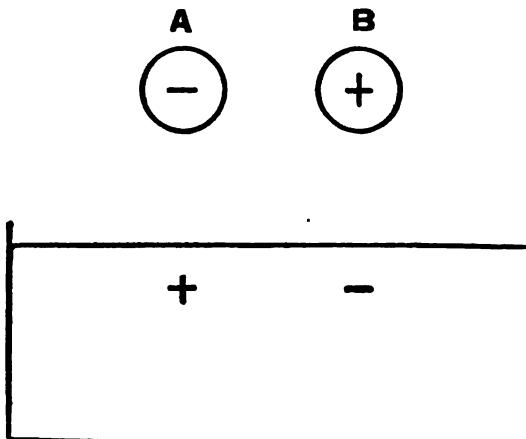
FIG. 19.
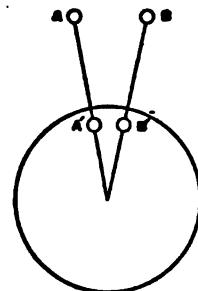
FIG. 20.

FIG. 19.—Diagram Illustrating the Part Played by a Dissociant when an Electrolyte is Immersed. A and B are the atoms of a molecule.

FIG. 20.—Diagram Illustrating Prof. J. J. Thomson's Theory of Electrolytic Dissociation, assuming that the atoms in a molecule are held together by electrical attraction.

is such a substance, it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in aqueous solution the forces between them are very much less than they are when the molecule is free and in a gaseous state."

Thus far we have considered only solutions of electrolytes in water. Water has therefore been the dissociant in all the cases which we have so far met with. Although water is the strongest dissociant known, there are other liquids capable of breaking down molecules when solutions are made in them. By strongest dissociant known we mean a solvent which breaks the largest number of molecules down into ions per unit of solvent volume. In very concen-

trated solutions of electrolytes we have a mixture of molecules and ions. As the dilution is increased the number of ions increases, for upon the addition of more water more of the molecules are broken down. The strong acids, bases, and salts are completely dissociated when a molugram equivalent is dissolved in 1000 liters of water. If we dissolve a molugram of a strong acid in 500 liters of water, we will have in solution molecules and ions. The solution conducts the electric current solely by the transport of the e'ectricity by the free ions. If we measure the conductivity of such a solution, we will, of course, obtain a certain conducting value. Now, what will be the effect of diluting the solution with water? With further dilution we get increased ionization up to the point where there are no molecules left, all having broken down into ions   We should expect the molecular conductivity of the solution to increase upon diluting with water, if the dissociation theory is true. *As a matter of fact, the molecular conductivity does increase up to the point where we have a gram-molecular equivalent dissolved in 1000 liters of water.* Now, water being the strongest dissociant known, all other solvents must be present in larger quantity to effect an equal dissociation. We will now give a table with the dissociants in order of their strength, and follow it by an easily performed practical experiment to show that dissociation increases upon dilution.

DISSOCIANTS IN ORDER OF POWER.

Water.
Formic acid.
Methyl alcohol.
Ethyl alcohol.

There are other dissociants, but the above are among the most common and generally employed. J. J. Thomson has also shown that the dissociating power bears a relation to the dielectric constants. This is in support of the theory of the electrical attraction between the atoms in a molecule. Having stated that dissociation and electrical conductivity increase upon dilution up to a point where we have the gram-molecule dissolved in 1000 liters of water, we will now test it by experiment.

PRACTICAL EXPERIMENT TO SHOW DISSOCIATION AND INCREASE IN ELECTRICAL CONDUCTIVITY UPON DILUTION WITH WATER.

In the following experiment there is developed a double and simultaneous indication of ionization, the appearance of a deep-red color on the one hand and the steady increase of electrical conductivity, upon the addition of water, on the other hand. The color change is dependent upon the well-known behavior of phenol-phthalein as a chemical indicator. To the characteristic color deportment of this interesting compound the conductivity method is simultaneously applied. The experiment as heretofore exhibite1 consists in merely noting the color change which is produced as follows: A small quantity of phenolphthalein is dissolved in ethyl alcohol and is poured into a tall glass lecture-jar to a height of about 5 centimeters. A few drops of ammonia water are then carefully added. There will be a slight momentary yellow coloration, which will immediately disappear upon shaking if too much ammonia water has not been added; if too much ammonia water has been added, add more alcohol. Now, chemists know that a colorless solution of phenolphthalein turns a beautiful red in the presence of a base. Here we have the phenolphthalein and the base, ammonium hydroxide, in alcoholic solution together, and no red color appears. Why? Ammonium hydroxide cannot show its basic properties until dissociated into the ions $\overset{+}{NH_4}$, $\overset{-}{OH}$, the isolated OH or hydroxyl producing such basic manifestations. Now, if we look at the table of dissociants, we see that ethyl alcohol is a very poor dissociant and is unable to break the ammonium-hydroxide molecules down into ions. Now, what will happen if we add some water? Water, as will be seen from the table, heads the list as the strongest dissociant known, and we should expect it to ionize the ammonium-hydroxide molecules if it be added. If the ammonium-hydroxide molecules are dissociated or ionized, we should expect the red color of the phenolphthalein to appear and become deeper and deeper as the molecules are broken up into active ions. This is just what happens. Upon the addition of water the color begins to appear and continues to get deeper and more decided as dilution continues. This is an odd sight, to see the addition of pure water to a faintly colored solution produce

a deeper and deeper color as dilution goes on. So much for the
color indication of dissociation on dilution. Now, molecules do
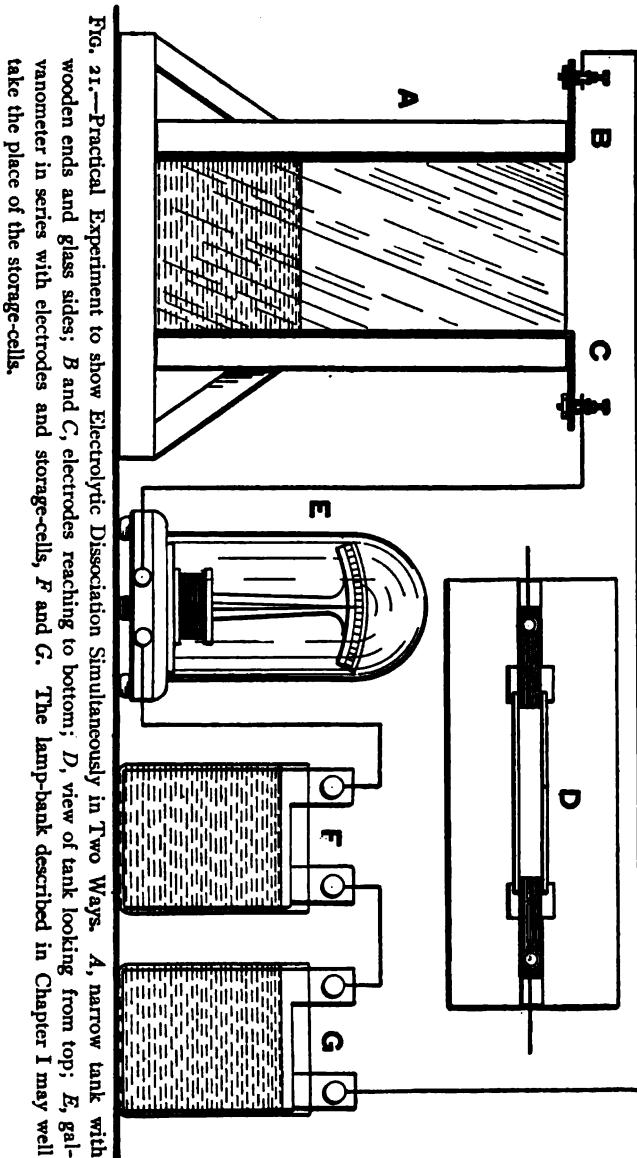
FIG. 21.—Practical Experiment to show Electrolytic Dissociation Simultaneously in Two Ways. A, narrow tank with wooden ends and glass sides; B and C, electrodes reaching to bottom; D, view of tank looking from top; E, galvanometer in series with electrodes and storage-cells, F and G. The lamp-bank described in Chapter I may well take the place of the storage-cells.

not conduct the electric current, and it occurred to the author to
perform this same experiment over again, but, instead of using the

glass jar, to employ a glass tank provided with electrodes and study
the conductivity behavior at the instant the color appears and follow
the conductivity behavior as the phenolphthalein deepens in color.
For this purpose a piece of apparatus was made as illustrated in
Fig. 21. With such a piece of apparatus we should not only ob-
tain the color reaction with an indicator, but an increasing con-
ductivity of the solution. The experiment is best and most forcibly
shown by first filling the tank with pure distilled water to the top,
having washed it out many times previously with distilled water to get
it perfectly clean, when there will be practically no indication upon the
galvanometer. The water is next poured out and the tank carefully
drained and dried as much as possible. It is then filled to the same
level with a solution of phenolphthalein in ethyl alcohol to which
some ammonium hydroxide solution has been added. This should
be colorless, as will be the case if not too much ammonia was added.
There will be practically no indication upon the galvanometer. We
have then separately tested the conductivity of the water and the
solution. Let us now see what the addition of water accomplishes.
For this phase of the experiment the phenolphthalein solution is
poured out, all but a small quantity. The writer usually leaves
solution in the bottom to a depth of about 5 centimeters. Water
is now very slowly added, when the red color begins to appear, and at
the same instant the galvanometer begins to show conductivity. As
the red color increases the electrical conductivity also increases, as
is plainly shown by the galvanometer. The dilution is continued
until the tank is full. The tank is constructed with a distance
between the glass sides of only 1 centimeter, and therefore requires
but a small volume of solution. The joint between the glass and
the wood is made in a deep groove by cement. We will now close
the present chapter with definitions of the new terms introduced.

Gram-molecule, or molugram.—Molecular weight of a compound
expressed in grams. The molecular weight of sodium chloride is
58.5. In order to use a gram-molecule of sodium chloride we
would weigh out 58.5 grams of the substance, for example.

Latent heat.—The amount of heat required to change the phys-
ical state of a body without changing its temperature. The heat
given out or absorbed when certain bodies change their physical
states.

Specific heat.—The amount of heat required to raise a gram of a substance one degree in temperature as compared with the amount of heat required to raise one gram of water one degree.

Calorie.—The unit of heat. The amount of heat required to raise one gram of water one degree in temperature. There are large Calories also, being 1000 times the small calorie, for convenience.

Heat exchange of calorimeter.—Error due to loss of heat by the calorimeter itself, by radiation, etc. To be determined by experiment with individual calorimeters by blank tests.

Elevation of boiling-point.—Often expressed in works on physical chemistry as "the lowering of the vapor-tension of the solvent."

"Bumping."—The liberation of steam with almost explosive violence from the smooth interiors of glass flasks when liquids are boiled in them. Prevented by introducing sharp points, as by the introduction of broken glass.

Dissociant.—A solvent that not only dissolves electrolytes, but breaks them down into ions at the same time. Benzene dissolves many electrolytes, but does not dissociate them, and therefore such a solution would be a non-conductor of the electric current.

Chemical affinity.—The attraction between the atoms in a molecule, whether due to electrical attraction or other forces.

Specific inductive capacity.—Dielectric constant. We owe to Cavendish (1771–81) the discovery of the fact that the amount of inductive effect which takes place through a dielectric is different for different substances.

Molecular conductivity.—Molecular conductivity of an electrolyte is equal to the specific conductivity of 1 cubic centimeter of the solution times the number of cubic centimeters containing a gram-molecular weight. $M = NS$, where M is the molecular conductivity, N the number of cubic centimeters of the solvent containing the gram-molecular weight or molugram of the electrolyte, and S the specific conductivity of a cubic centimeter of the solution.

CHAPTER IV.

NOVEL EXPERIMENTS IN "ELECTROLYTIC INDUCTION."

As it is the purpose of the first few chapters of this work to acquaint the student with the constitution and behavior of electrolytes under various conditions, such effort would fail should we neglect to touch upon the electrostatic and electromagnetic deportment of substances in solution. Having dealt with electrolytes theoretically and experimentally, and learned the fundamental laws upon which their behavior depends, we will be in a position to take up the practical work which is to follow in the later chapters, and from the subject of electrochemistry as a science touch upon electrochemical engineering as an art. We are, therefore, acquainting ourselves with electrolytes, the theories upon which they are based, and their capacities as electrical conductors. We shall also study electrolytes as producers of the electric current but this phase of substances in solution is best left until a little later. The first experiment illustrating the effects of electrical induction upon an electrolyte as given in Fig. 22 was designed by Wilhelm Ostwald, Professor of Chemistry in the University of Leipzig, and one of the most distinguished physical chemists Germany has ever produced. Prof. Ostwald's experiment has for its object to prove the existence of "free ions" in an electrolyte, and to show that they actually migrate and carry the electrical charges upon them. The author became much interested in Ostwald's work, and repeated the experiments for himself, continuing the research still farther, as will be described in the present chapter, developing what may be termed "electrolytic induction." Let us first take up the experiment of Ostwald referring to the illustration. In the experiment with potassium chloride, Ostwald writes as follows: "The following consideration may serve to remove the last doubts as to the validity of the assumption of free electrically charged

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atoms of chlorine and potassium. Imagine two insulated vessels, *B* and *C*, filled with a solution of potassium chloride and electrically connected by means of the siphon *D*. Let a negatively charged body be brought near *B*, remove the siphon, and lastly the charged body *A*. Then, as is well known, *B* remains positively electrified, and *C* negatively electrified. Now, according to Faraday's law, the electricity in electrolytes can only move simultaneously with the ions. Consequently, if an excess of positive electricity is present in *B*, there must also be an excess of free potassium ions, i.e., of potassium
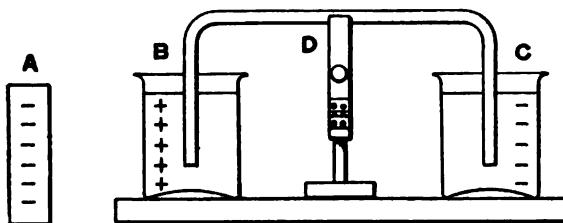
FIG. 22.—Prof. Ostwald's Experiment in Static Induction to Show the Presence of "Free Ions." *A*, negatively charged body; *B* and *C*, beakers filled with a solution of potassium chloride; *D*, siphon-tube filled with the same solution and joining the two beakers.

atoms, by the electricity of which the charge is determined. If the electricity is conducted away, * the potassium assumes the ordinary form, and acting on the water of the solution develops hydrogen, which can be collected in suitable apparatus and tested. Similar considerations hold good for the chlorine in the vessel *C*. It is consequently not only conceivable that the ions in an electrolytic solution move about with electrical charges, otherwise quite free, but solutions may be prepared which contain an excess of any ion we choose, e.g., an excess of potassium. The assumption that electrolytes contain free ions is not only possible but necessary."

This experiment as originally proposed by Ostwald was not at all practical, for the quantity of hydrogen gas liberated was so small that it could not be seen. The liberation of hydrogen is based upon the following simple equation:

$$2K + 2H_2O = 2KOH + H_2.$$

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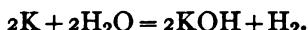
* By inserting in the beaker *B* a platinum wire to earth.—N. M. H.

The experiment was eventually modified by Profs. Ostwald and Nernst, the latter being also one of the most brilliant German physical chemists of the times. This experiment shows to the eye the liberation of hydrogen under similar conditions of static induction, and is a practical illustration of great beauty. The arrangement of the apparatus for this experiment is shown in Fig. 23. At *A* we have the positive knob of a static electrical machine connected by a tinsel
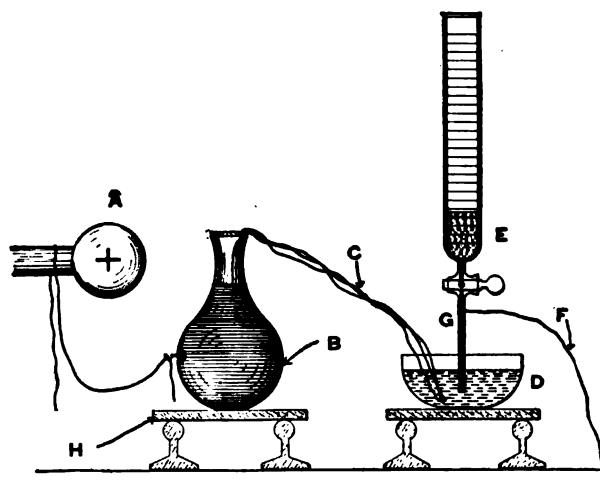
FIG. 23.—Ostwald and Nernst's Experiment in Static Induction to Show the Presence of " Free Ions." *A*, positive knob of electrical machine; *B*, glass flask covered with tinfoil; *C*, wet strings connecting the glass flask and the vessel *D*, both containing dilute sulphuric acid; *E*, burette drawn out into a fine capillary, *G*, through which the side of which the platinum wire, *F*, is fused; *H*, glass plate on glass insulators.

cord or small metal chain to the little hook on the tinfoil covering of the glass flask *B*. This flask is filled with dilute sulphuric acid and is thoroughly insulated upon a glass or hard rubber-plate resting upon small insulators also of glass. Cords or strings wet with the same dilute sulphuric acid dip into the flask and connect with the vessel *D* also containing some of the same sulphuric-acid solution, and being insulated in a similar manner. The glass burette *E* has been drawn out into a long and fine capillary *G* through which a fine platinum wire is fused and which turns to earth. Now what happens when the electrical machine is put into operation? The

tinfoil coating being electrically connected with the electrical machine becomes positively charged, which, acting through the glass of the flask, attracts and holds a corresponding amount of negative electricity, while the positive is repelled. The positive electricity, or, as we believe, the positive ions, which in this case are hydrogen (H_2SO_4 ionizes into $\overset{+}{H_2}\ \overset{-}{SO_4}$) is repelled through the moist cord which leads to the vessel D and the capillary of the burette filled with the acid and water to a height of a few centimeters, when it meets with a little column of mercury at G connected to earth. This mercury was drawn up into the capillary by placing it in the bottom of the vessel D, when some of the dilute sulphuric-acid solution was allowed to follow. Now the hydrogen ions are repelled through this system and are discharged when they reach the grounded mercury. They then become ordinary atoms of hydrogen, and may readily be seen in the capillary. On starting the electrical machine the experimenters observed a rush of tiny bubbles of gas through the mercury at G, collecting at the top under the glass stop-cock, the $\overset{-}{SO_4}$ ion being held by the positive attraction on the outside of the flask B. Here we have a very beautiful experiment based upon an induction phenomenon. The experimenters also conducted a most elaborate quantitative research upon this phenomenon, to ascertain if the amount of hydrogen set free at G corresponded to that calculated from Faraday's law, and found within the limits of experimental error that it did. We shall take up Faraday's law and the subject of electrochemical equivalents in a later chapter, but at the present time it is only wise to state that all ions have definite capacities for the electrical charges according to their valencies. Knowing the electrochemical equivalent of hydrogen, for example, it would be an easy matter to calculate what mass, or what volume of hydrogen, would be set free by a given quantity of electricity. The experimenters referred to employed such a course in checking the above experiment quantitatively. So much for the experiment of Ostwald and Nernst, depending upon the liberation of hydrogen as proof of the migration of free ions. Fig. 24 illustrates the author's modification of this experiment based upon the use of the reflecting galvanometer as a chemical indicator, to prove that ions had migrated under the influence of static induction. Gaugin, and later Prof.

Kuester, employed the reflecting galvanometer as a chemical indicator, and the use of such an instrument for detecting acids and bases
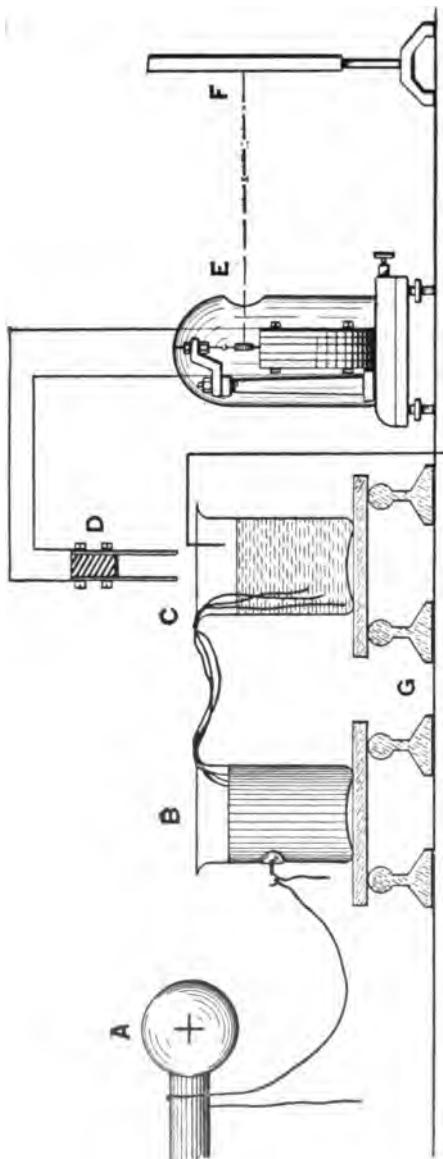


FIG. 24.—Hopkins's Experiment in Static Induction to Show the Presence of "Free Ions." A, positive knob of electrical machine joined to tinfoil covering of the beaker, B, by means of a small metal chain; C, similar beaker without tinfoil covering, but insulated on glass at G; both beakers are filled with potassium-chloride solution and are joined by wet cords; D, platinum electrode attached to hard-rubber insulator; E, delicate reflecting galvanometer; F, scale of reflecting galvanometer.

will be described before we describe the author's experiment. To quote from Gaugin's work we have the following: "Electromotive

Force of Platinum in Contact with Acidulated or Alkalinized Water:
Two plates of platinum were immersed in acidulated water for
some time. One being withdrawn, washed in distilled water, and
returned, was found to be negative. Electromotive force = 0.0136
volt. Water alkalinized with KOH was then substituted. The
washed and returned plate was found to be positive. Identical
results were obtained with plates of platinized platinum. It is
possible to recognize by this means whether a liquid is neutral, or
acid or alkaline, even when its reaction is so feeble as not to affect
test-papers."

Now the author's experiment consists in operating the electrical
machine, when the tinfoil coating of the beaker B will be positively
charged and will hold the negative ions of the potassium chloride
$\overset{+}{K}\,\overset{-}{Cl}$, which, as may be readily seen, are chlorine ions, and will repel
the positive ions which are potassium through the moist cord into the
beaker C, where they may be discharged, after the removal of the wet
cord, by the platinum wire shown at the right of the beaker   Upon
discharging the potassium ions they become potassium atoms and
react with the water as before $2K + 2H_2O = 2KOH + H_2$, forming
potassium hydroxide and setting hydrogen free. This experiment does
not attempt to show migration by the setting free of the hydrogen,
but by the formation of the alkali, or base, KOH, potassium hydroxide.
To do this the reflecting galvanometer is employed. It would be
expected that the chlorine ions could be discharged in the same
manner and their presence shown by a drop or two of silver-nitrate
solution. Although there is little doubt of their being discharged in
the same manner, the minute quantity of chlorine present would not
suffice to give a chemical precipitation of silver chloride. Perhaps
if the electrical machine was allowed to run for several days, a slight
opalescence might be observed when a drop or two of silver nitrate is
added. When we complete our studies of Faraday's law involving
the electrochemical equivalents we will be in a position to appreciate
how few chlorine ions would migrate under such circumstances as
we have in this experiment. All ions carry very great electrical
charges, and we know as physicists that there is very little quantity
of electricity to be had from a static machine. The electricity from
a frictional machine is *almost all potential difference!* The amperage
in a current from a static machine is so small as to be detected and

measured only by very special means.   Now a few ions are capable
of carrying many amperes, as we shall see later, and it is not sur-
prising under the circumstances that our static charges have been
carried by very few ions indeed.   We will now leave experiments
with static induction and study the effects of magnetic and galvanic
induction upon electrolytes.   All the following experiments are
based upon the original researches of the present author, and are
now published for the first time.   It occurred to the writer to com-
pare electrolytes with metallic conductors when under the influence
of magnets and electric currents in neighboring conductors, to see if
inductive effects and inductive currents were produced.   Will a
magnet induce a current of electricity in an electrolyte as it does in a
metallic conductor?   This question is not touched upon in the treatises
in physics or chemistry, and it was therefore resolved to answer the
question by experiment.   Fig. 25 shows the first comparatively
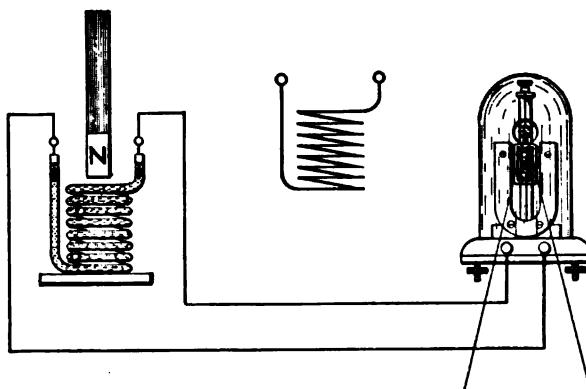
FIG. 25.—Experiment to Learn the Effect of a Magnet upon a Coil of Electrolyte.
The central figure represents a coil of wire of equal resistance and dimensions,
which may be substituted for the coil of electrolyte.

rough plan for learning whether a magnet will induce an electric
current in a coil of electrolyte as it does in a coil of wire.   We have
here a sensitive reflecting galvanometer at the right to show any
induced current.   As a matter of fact a magnet does induce a current
of electricity in the electrolyte and causes the galvanometer to indi-
cate the same.   The coil of wire represented in the center was made
of equal dimensions with and substituted for the coil of electrolyte
to ascertain if the effect was quantitatively the same.   The coil of

electrolyte consisted of a glass tube filled with a dilute solution of sulphuric acid. It was necessary to introduce in series with the metal coil some additional resistance, which was of a non-inductive type, in order to obtain comparable conditions, as the coil of electrolyte had a much higher ohmic resistance than the coil of wire. The deflection of the galvanometer proved to be the same in both cases. As it was an impossible matter to place the magnet in the two respective solenoids in exactly the same manner and at exactly the same time, the experiment as illustrated in Fig. 26 was conducted. Here we have at the left a soft-iron bar running horizontally through a coil of insulated wire which is in series with a storage-battery, the terminals of the wire being free for connection with a contact key which may be closed uniformly any number of times. Next to the coil we have a glass coil filled with any good electrolyte in solution, into which the terminal wires (which must be of platinum) of a reflecting galvanometer dip. At the extreme right we have a coil of resistance wire of equal proportions and equal number of turns as in the glass coil, and in series with it a rheostat of the non-inductive type, for bringing the wire to the same resistance as the coil of electrolyte. Of course some wire of high resistance must be used, such as is employed in resistance sets, in order that we will not have to depend upon much outside resistance, as by the use of the rheostat. The coil of alloy wire may now be substituted for the coil of electrolyte, and by means of the key and storage-battery, operating the electromagnet, we can produce the same number of magnetic lines of force in just the same way and in the same time as we did in the case of the coil of electrolyte. Experiments with such a piece of apparatus gave the same deflections of the galvanometer with a coil of electrolyte as they did with a coil of alloy wire. We can then think of the free ions being migrated by ordinary magnetic induction so common to all students of physics and electrical engineering. Let us now study the effect of an electric current upon a magnetic needle while traversing an electrolyte. For this purpose set up a piece of apparatus like that represented in Fig. 27. Here we have a glass tube about a meter in length by about a centimeter in internal diameter, bent up at the ends as indicated. This is filled with dilute sulphuric acid, and is provided with platinum electrodes with *loose-fitting stoppers*. The tube is supported on two laboratory stands above a delicate compass-

needle with a graduated arc or scale. There are also two upright
standards provided with insulators between which an alloy wire is
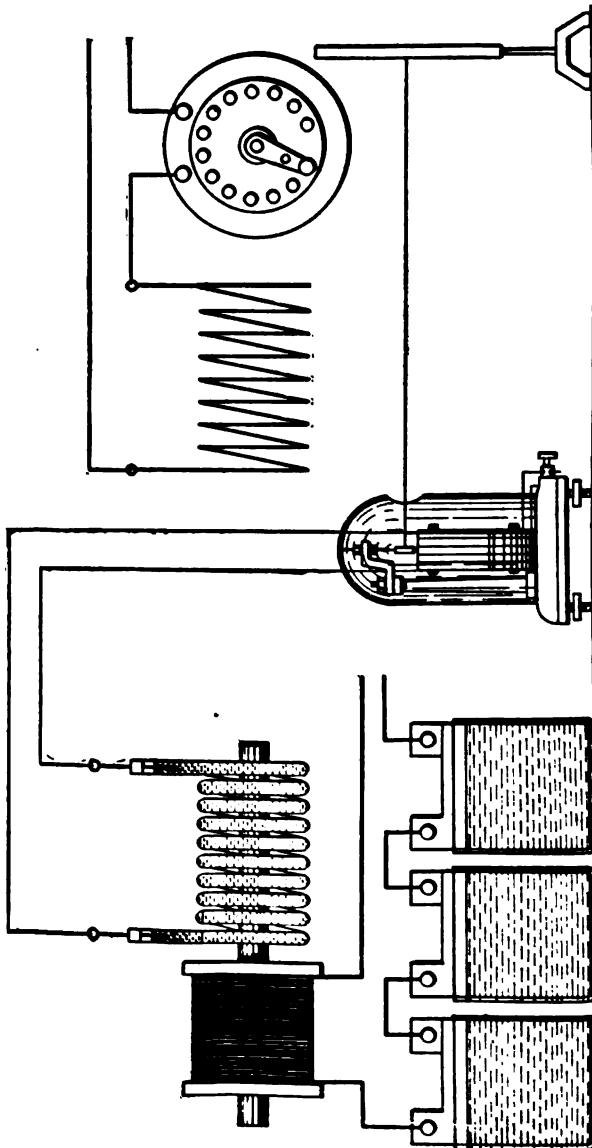
Fig. 26.—More Refined Method of Determining Quantitatively the Effect of a Magnet upon a Coil of Electrolyte Compared with a Coil of Wire of Equal Dimensions and Equal Ohmic Resistance.

stretched taut at the same height as the glass tube, so one may be
substituted for the other above the magnetic needle. The magnetic

needle is represented upon an adjustable stand in order that it may always be brought to exactly the same distance below the wire and electrolyte respectively. The measurement must be made from the center of the wire and electrolytic tube respectively. Below in the same illustration we have a plan of the apparatus, looking down upon it. It will be readily seen with such an arrangement how the wire
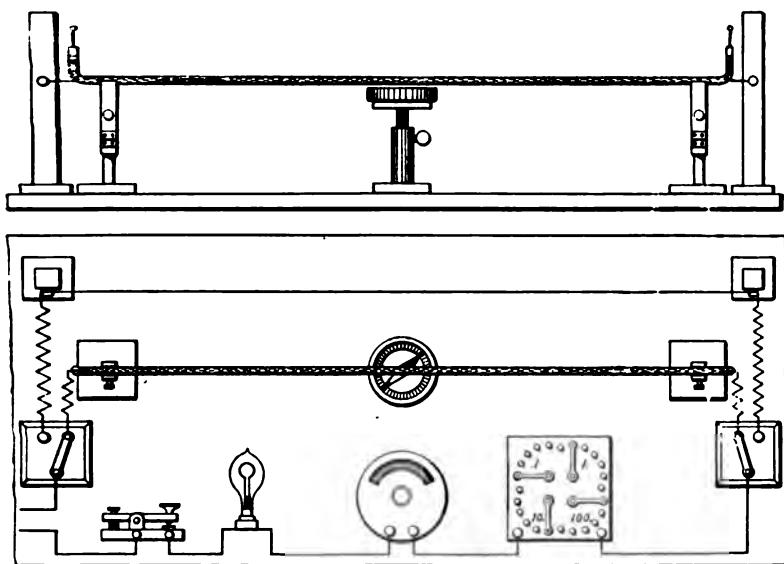
FIG. 27.—Experiment to Show the Effect of Electrolytic Conduction upon a Magnetic Needle. The experiment is so designed that a wire carrying an equal current of electricity may be substituted for the electrolyte and the deflection of the magnetic needle quantitatively compared. We can throw in series with the electrolyte or wire at will the lamp, ammeter, and variable rheostat which join to a lighting circuit or storage-battery. The arrangement of the two switches at either end will make this clear.

may be quickly substituted for the electrolyte, and how the electric current may be controlled and made to flow through the electrolyte. In conducting this experiment the student will be impressed with the greatly superior conductivity of metals and even high-resistance alloys over electrolytes. The result of such a carefully conducted experiment will show that the magnetic effect of electric currents traversing electrolytes is quantitatively the same as electric currents of equal strength traversing conductors of the first class. The thought-

ful student will be likely to ask why the effect is just the same when we have positive ions going to the cathode carrying positive electrical charges and negative ions going to the anode carrying negative electrical charges. The only answer that can be given is that a negative ion traveling from right to left tends to turn the magnetic needle in the same direction as a positive ion does traveling from left to right. We know that the same current traversing a wire will turn a magnetic needle to right and left respectively, according to its position above or below the needle, and that we can greatly increase the magnetic effect by carrying the wire over and under the needle a number of times. We may say that a positively charged particle, or ion, produces the same effect upon a magnetic needle, traveling from right to left, as a negatively charged ion does traveling from left to right. The author has designed an elaborate experiment to show this by a rapidly running band of pure silk ribbon, upon which are pasted little tinfoil disks. The band may be run right-handedly under a suspended magnetic needle, with positive static charges upon the tinfoil disks and the deflection and direction of the magnetic needle noted. The direction of the band may then be reversed, and the disks be charged negatively, when the deflection and direction of the needle are again noted. The little disks are charged by passing under and touching a tinsel brush connected with either pole of an electrical machine of the static type. This is a mechanical representation of migrating ions in opposite directions. Owing to the small quantity charge of electricity upon the disks which were placed about 3 centimeters apart the ribbon was run at high speed. The drums over which the ribbon ran were supported upon solid glass axles to insulate the same. As a matter of fact ions travel very slowly, but carry very large charges of electricity. In the running ribbon we have very small charges of electricity, and therefore to obtain the same magnetic effects we should be obliged to drive the ribbon and little tinfoil disks at very high speed. The magnetic needle must therefore be protected from resulting air-currents in some suitable manner. Having seen the effects of electric currents passing through electrolytes on magnetic needles, it remains only to observe the effect of electric currents passing through electrolytes on masses of ordinary soft iron. Fig. 28 illustrates a simple experiment to measure the "magnetic pull" upon a soft-iron bar, if such

pull exists. At the right-hand side of 'he diagram we have an analytical ba ance with the left pan removed in order that we may suspend the bar of soft iron to be experimented upon. Directly under the iron bar is a block of wood or other suitable support for the glass coil of electrolyte. The platinum electrodes which dip into this electrolyte connect through an open scale, or delicate ammeter, in series with the variable rheostat and lamp-bank. The lamp-bank described in the first chapter of our series may be used. We can now by this arrangement admit current to the electrolytic coil, read the current in amperes, and weigh the magnetic pull to a great degree of accuracy. Substituting the alloy coil, we can, by means of the lamp-bank and variable rheostat, cause the same current to flow through
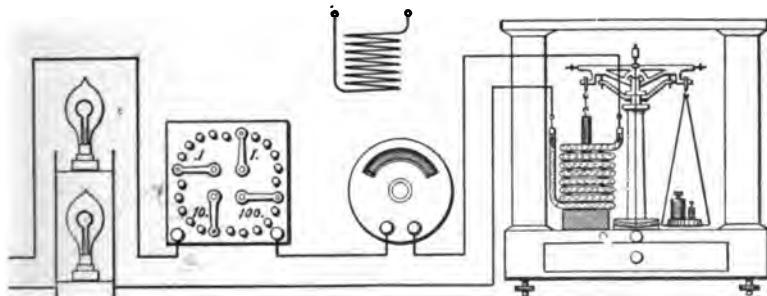
FIG. 28.—Experiment to Show and Quantitatively Measure the Magnetic Pull of an Electrolyte Carrying an Electric Current. At the left is an ammeter, a variable rheostat, and a lamp-bank; above the ammeter is a coil of alloy wire for substitution purposes.

the alloy coil and weigh the pull. As a result of scores of tests of this character the author found the pull to be just the same with an electrolyte as it was with a wire carrying the same current. Of course it goes without saying that the convolutions, and consequently the ampere-turns, were the same in both cases. For accurate work it must be impressed, however, that a rather fine wire of high specific resistance must be employed for the conductor of the first class. Otherwise the resistance of the wire coil will be so much less than the electrolyte that we must turn in a great deal of outside resistance through the agency of the rheostat. Perhaps the most interesting of all these experiments is that illustrated in Fig. 29, which has been termed a demonstration of "electrodeless conduction." Here we have simply a closed system, an electrolyte without the customary

electrodes for giving and taking the electric current.   Let us refer
to the diagram and describe the method of showing this remarkable
phenomenon.   The illustration represents an original experiment of
the author performed a number of years ago, but like those preceding,
it has never been published.   *A* represents an alternating-current
generator connected to a coil of insulated wire on the spool which
encloses a soft-iron bar.   This soft-iron bar passes into a glass coil
of tubing containing dilute sulphuric acid, and is joined through
two straight glass tubes about a meter long to a second glass coil
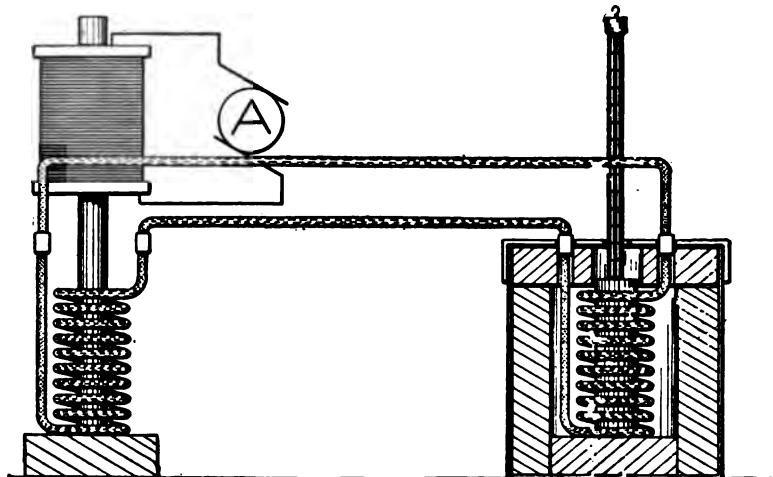
FIG. 29.—Experimental Demonstration of " Electrodeless Conduction." *A* repre-
    sents an alternating-current dynamo connected to a coil of insulated wire; through
    this coil a soft-iron bar is passed which enters a glass coil filled with an electro-
    lyte; this glass coil is connected by glass tubes with a second glass coil which is
    placed within a calorimeter; a cylinder of thin soft Russia iron is placed within
    this second coil, which in turn received a very sensitive thermometer.

filled with the same solution.   This second coil of electrolyte, however,
is incased within a calorimeter made from a common pasteboard
muff-box, lined within with hair felt, as indicated by the diagonal
lines.   Within this coil is placed a small cylinder of thin Russia iron,
which receives in turn and incloses the bulb of a sensitive thermometer,
like those employed in our previous calorimeter work.   One of Beck-
mann's thermometers with arbitrary scale and reservoir at the top is
an excellent type.   The cover is placed on the calorimeter, and after
equilibrium has been established the thermometer is read and the

dynamo started. The temperature will slowly rise when within the little iron cylinder. If the cylinder is removed the mercury in the thermometer will fall again, and rise once more upon lowering the cylinder. What part does the little cylinder play? It is well known to all physicists and most electricians that iron heats up when it is magnetized first in one direction and then in the other by the alternating current. This heating of iron by an alternating current under such circumstances is called "hysteresis." Here we have the heating of the little iron cylinder by being rapidly magnetized first in one direction and then in the other, which gives us proof that the closed system, without any electrodes whatever, is conducting the electric current. On breaking the system anywhere, with the dynamo still in operation, the heating ceases. Here we have undoubtedly the ions driven first in one direction and then in the other, reversing their magnetic effect with their direction. If we could insert our thermometer in the electrolyte itself, we would probably get a heating effect due to the "friction" of the ions among themselves. Fig. 30 illustrates a plan for carefully studying the effects of alternating currents upon electrolytes of different composition. The wiring and apparatus is so arranged in this experimental study as to allow of supplying alternating currents of the same energy value, but of various frequencies. It has been shown by the writer with such an experimental apparatus that the frequency of the alternations, everything else remaining the same, has a decided effect upon electrolytes. Only a very few years ago little had been done with the alternating current as applied to electrolytes, and nothing involving alternating currents with change of frequency. By "frequency" we mean the number of double reversals of the current per second. The frequency varies in practice between 25 and 150. The term "period" used in connection with an alternator denotes the time elapsing between one complete reversal of the current. Now if we have free ions in solution which carry the electric current, they must move back and forth to some extent under the influence of an alternating current. In other words, they must oscillate. Now by varying the frequency of our alternations we vary the rate of oscillation of the ions, and if the heating is due to friction between the ions, the heating should be greater at higher frequencies than with low frequencies. Such was found to be the
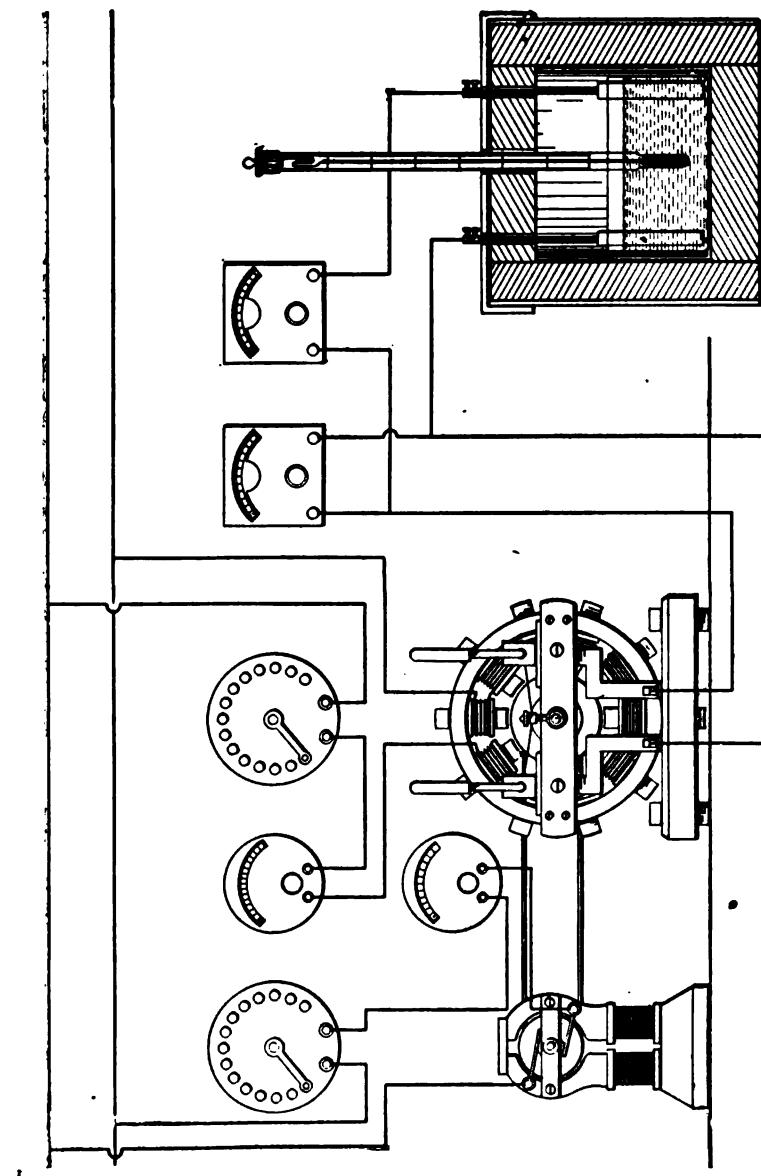
FIG. 30.—Apparatus to Study the Heating Up of Electrolytes by Alternating Currents at Various Frequencies. At the extreme right, calorimeter, electrolyte, electrodes, and Beckmann thermometer; alternating-current ammeter and voltmeter in connection with leads; alternating-current generator with separately excited fields, and rheostat for varying strength of same. Electric motor at extreme left in series with rheostat for controlling speed, and ammeter for reading current taken.

case, the energy value of the alternating current being kept the same. By a glance at the last illustration we can readily see how the frequency may be changed without altering the energy value of the current. We can strongly excite the fields of the alternator by admitting a heavy current through the rheostat and driving the alternator by means of the motor at low speed, when we will obtain an alternating current of low frequency and of a definite energy value. We can experiment with this arrangement. We can now turn in our rheostat and admit a feeble current to the fields of the alternator, and by driving the armature at a high speed we will be able to obtain the same energy value for the current, but at high frequency. Experiments were also conducted with electrolytes of various compositions, that is, with light and heavy ions present respectively. The electrolytes consisting of light ions invariably heated up quicker than electrolytes with heavy ions. This can only be explained on the ground of inertia. The lighter ions travel through the greater distances when oscillating, and therefore collide a greater number of times. The heavier ions, because of their greater inertia, do not respond so readily to the alternations, and therefore move through a lesser distance. They consequently do not meet with so many collisions, and the friction is reduced. This of course is theory, but the fact of experimental investigation remains that the lighter ions cause a more rapid heating than heavy ions, and that all electrolytes heat up more quickly with alternating currents of high frequency than they do with alternating currents of low frequency. It only remains for us to find a theory to account for the facts.

CHAPTER V.

THE VELOCITY OF ELECTROLYTIC CONDUCTION.

EXPERIMENTS WITH A HIGH-SPEED SPECIAL CHRONOGRAPH CAPABLE OF DIVIDING A SECOND INTO A MILLION PARTS.

Absolute Velocity of Ions.

It will be recalled that in the preceding chapter ions were made to travel by induction. In the experiment with the electrical machine the two vessels connected by means of the wet string, and the capillary, the electrostatic charging of the electrolyte took place at once. In other words, as soon as the electrical machine was started, bubbles of hydrogen gas made their sudden and immediate appearance within the capillary. Now, as a matter of fact, the bubbles of gas would make their appearance at once, whether this wet-string conductor was long or short. The electrical conduction would be instantaneous, and yet we will learn a little later in the present chapter, under the heading "Absolute Velocities of the Ions," that the ions themselves move very slowly and have different velocities. How can we account, therefore, for the instantaneous conduction of an electrolyte, when the ions which carry the electricity upon them move very slowly and have their respective velocities? We can only account for the facts in such an experiment by attributing the instantaneous conduction to be due to free ions already present about the electrodes. Fig. 31 represents an experiment of Prof. Ostwald to show the instantaneous electrical conduction through electrolytes. Here we have a glass tube about 50 centimeters long and 1 centimeter in diameter bent at right angles at the ends and enlarged into cylindrical terminals as shown. At the left we have a stick of chemically pure zinc supported in position by a cork. At the right we have a bent-tube manometer con-

taining a little colored water, supported by a good tight cork also. At the bend on the right a platinum wire is fused in place to act as the other terminal or electrode. The tube is filled with dilute sulphuric acid. Upon connecting this piece of apparatus with a battery, motor-generator, or lamp-bank as described in the first chapter, making the zinc the anode and the platinum wire the cathode, bubbles of hydrogen appear instantly upon the platinum wire, and a pressure is indicated upon the water-gauge. The instantaneous appearance of bubbles of hydrogen with the closing of the contact
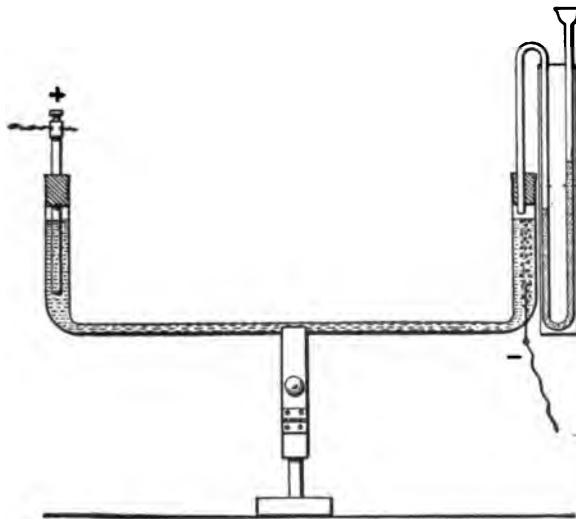
FIG. 31.—Prof. Ostwald's Experiment to show Instantaneous Electrical Conduction through an Electrolyte.

key in series with the source of electricity goes to prove the presence of free ions already about the electrodes. These free ions merely give up their charges and escape upon completing the circuit. Now, if it was necessary for the electric current to first decompose or break up the molecule of sulphuric acid, then the two atoms of hydrogen replaced by the zinc in the SO_4 radical, must have traveled to the platinum-wire cathode through the tube, which is 50 centimeters long. Now there are experiments, as we shall see at the close of this chapter, to determine the absolute velocities of ions, and measurements upon the velocity of the hydrogen ion show that it would require a long time for hydrogen ions to travel through a

tube 50 centimeters long. Now, hydrogen appears at once upon closing the circuit, and we must attribute the immediate response or conductivity of the solution, to free ions already around the electrodes in readiness to discharge their electricity. Although this experiment of Prof. Ostwald is one of great interest, it struck the present writer as being very crude and rough and capable of great improvement. It does not answer many vital questions. For example, do all electrolytes conduct with the same velocity? In other words, will an electrolyte consisting of heavy ions respond or conduct as quickly as an electrolyte consisting of light ions? Will all electrolytes conduct as quickly as a metallic conductor? This appeared to be neglected as a piece of research work; and with a view of comparing different electrolytes with each other both in solution and in igneous fusion, and in comparing electrolytes with metallic conductors, the special high-speed chronograph was designed and built as illustrated in the following drawings. Through the agency of this chronograph, a dynamo current was compared with the current from a set of accumulators, and light thrown upon such questions as mechanical movement of ions of different weights, involving the question of inertia. Let us first compare electrolytic conduction in an electrolyte with metallic conduction, for if the two act in the same time, the evidence in favor of free ions is strengthened. Fig. 32 outlines in diagram the chronograph cylinder and the electrolyte and wire respectively. Here A represents the electrolyte in the glass tube, and B the parallel metallic conductor. C is a rheostat in series with the metallic conductor to bring the same to an equal ohmic resistance with the electrolyte. D represents a delicate ammeter in series with the electrolyte and the electromagnet E of the chronograph. F represents in dotted lines the same ammeter shifted in series with the metallic conductor and the electromagnet G of the same chronograph. H illustrates a double switch for simultaneously closing both circuits after the resistances of the two have been balanced or made carefully equal to each other. By revolving the chronograph cylinder and closing the switch, the two electromagnets will strike the paper band upon the chronograph cylinder and draw records by means of soft lead-pencil points. The chronograph and magnets must first be most carefully calibrated on one and the same circuit by connecting the

magnets in series with each other, thereby supplying a common
current of electricity, and adjusting their springs and striking dis-
tances until a current of common value will cause both magnets to
strike upon the rapidly revolving cylinder at the same instant.   This
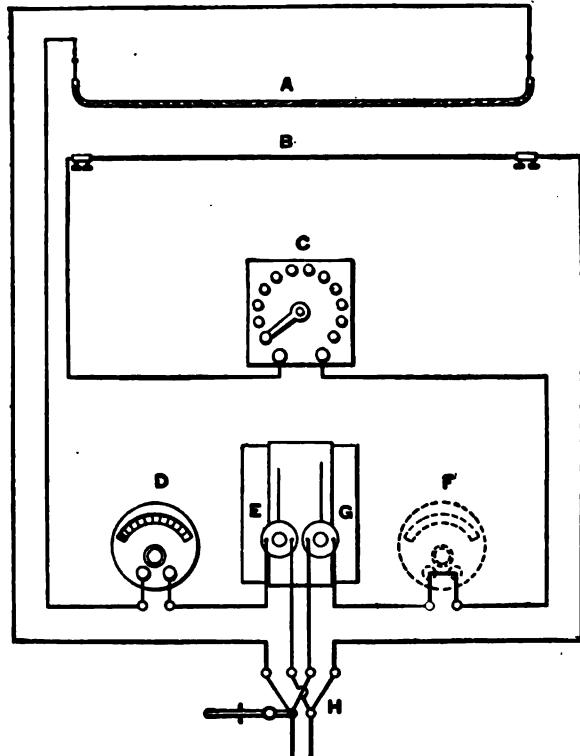
FIG. 32.—Diagram of Author's Method of Studying Time Required for Electric Cur-
rents to Traverse Electrolytes, and to Compare the Time with that Required by
Metallic Conductors.   A, electrolyte; B, parallel wire; C, rheostat for balancing
resistance of wire to that of electrolyte; D, mill-ammeter in series with electro-
lyte and magnet E; at F the mill-ammeter is shown shifted in series with wire
and magnet G; H, double switch for closing both circuits simultaneously.

can most easily be seen by the pencil records.   When by careful
experiment and adjustment the two electromagnets strike "abreast"
upon the flying cylinder, which is driven by a high-speed elecrtic
motor, the series connection is changed and each electromagnet
is placed separately in circuit with electrolyte and wire respectively,
previously made of equal ohmic resistance.   The lines upon the-

cylinder in this drawing illustrate the appearance of the pencil record when the cylinder is driven at moderately high speeds. A photograph of such a chronograph is given in Fig. 33, where an electric motor is directly connected by means of a flexible coupling to reduce vibration. It was soon found, however, with such a
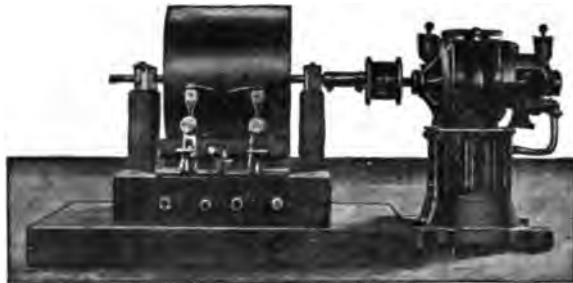
Fig. 33.—Photograph of Simple Drum High-speed Chronograph Direct Connected to Electric Motor.

simple chronograph cylinder, when driven at very high speeds, that the pencil records were drawn all the way around, and it was impossible to see where the contacts were first made. It became
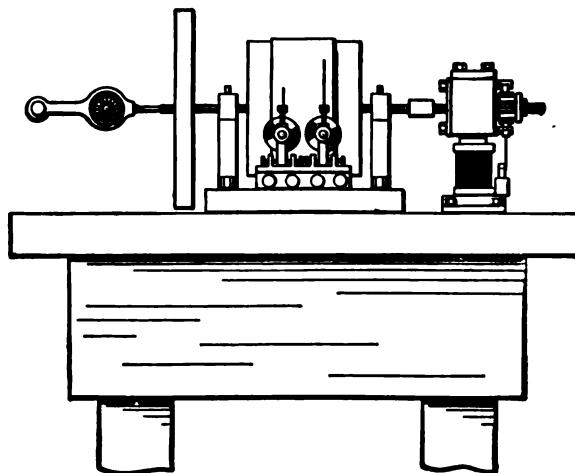
Fig. 34.—Rear View of Electrochronograph provided with Electric Motor, Balance-wheel, and Revolution-counter. This instrument is a modification of that shown in Fig. 3, as it drives a long band of paper for receiving record.

necessary to expand the chronograph by driving a long band of paper. Figs. 34 and 35 will make the plan clear. In Fig. 34 the

end of the chronograph cylinder is again shown, with its electric
driving motor at the right, and with a heavy balance-wheel to steady
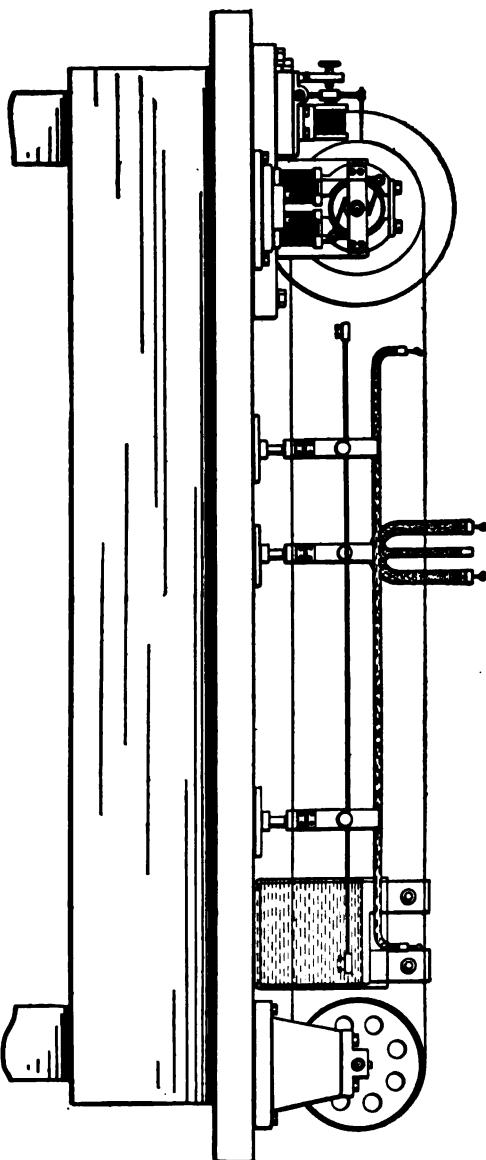
FIG. 35.—Side View of Electrochronograph Cable for Dividing a Second into Fifty Thousand Parts in Connection with an Electrolyte for Studying the Velocity of Electrolytic Conduction. The paper record-band is shown passing over the loose drum-wheel at the extreme right.

its rapid motion at the left. A revolution counter is also depicted
at the extreme left, pressed against the shaft of the chronograph

cylinder. This revolution counter was afterward moved to the shaft of the pulley at the far end of the band, as being a fairer place, for in case there was a slight creeping of the band upon the chronograph cylinder, there would be no error introduced from this cause. Fig. 35 illustrates a side view of this special form of band chronograph, showing its band and supporting drum-wheel at the far end of the work-table over which it runs. The arrangement of the marking-pencils and electromagnets is made clear in this illustration. Upon the work bench or table are the electrolyte and wire respectively, together with a cell or storage battery and a special form of U tube used for various conduction experiments with electrolytes. This particular chronograph revolves at the rate of two thousand revolutions per minute, and it will be seen that the slightest "lag" in conductivity in either circuit, when the two are closed simultaneously by a proper key, will be shown accurately and quantitatively upon the moving band. With this arrangement, as will be seen from the following mathematical exposition, a second may be divided into one hundred thousand parts; and by higher speeds, the second may be laid off and divided into a million parts, dependent upon the behaviors of the various conductors experimented with. The diameter of the chronograph cylinder being 15 centimeters, we can take this as a basis upon which to start the calculation.

$$3 \cdot 14159$$
$$15 \text{ cm. diameter}$$

$$\overline{}$$

$$1570795$$
$$314159$$

$$47 \cdot 12385 \text{ cm. circumference}$$

With 2000 revolutions per minute, we have $47.12385 \times 2000 = 94247.70$ centimeters per minute. The space traveled during one second is therefore

$$60)94247.70(1504.1283 \text{ cm.}$$

In 1/10 second   we have 150.41283 cm.
In 1/100 second   "   15.041283 cm.
In 1/1000 second   "   1.5041283 cm.
In 1/10000 second   "   .15041283 cm.

Working with a chronograph of still higher speed, the cylinder being driven by a two-horse-power motor belted up for speed, the scale upon the flying band was of course still more open, and allows of determinations to be made to 1/100,000 and even 1/1,000,000 of a second. A tabulated length of spaces upon this high-speed band is as follows up to hundred-thousandths of a second. The figures are as follows:

Cm. Circumference.	Rev. per Min.	Cm. Traveled.
47.12385	× 10000 =	471238.5 cm. per min.

$$60)471238.5(7853.97500 \text{ cm. per second.}$$

In 1/10 second	we have	785.397500 cm.
In 1/100 second	"	78.5397500 cm.
In 1/1000 second	"	7.85397500 cm.
In 1/10000 second	"	.785397500 cm.
In 1/1000000 second	"	.0785397500 cm.

For higher speeds still and correspondingly more minute subdivisions of the second, a chronograph rigged like that shown in Fig. 36 was experimented with. Here we have an electrolyte 50 feet long in the glass tube arranged like a steam-radiator, and the chronograph cylinder driven at enormous speed by the multiplying system of belting to the countershaft, etc. The telephone-receiver, cell of battery, induction-coil, and resistance set depicted here were employed to balance the resistances, instead of the ammeter employed in the slower-speed design of instrument. The method of measuring resistances by means of the telephone and induction-coil is known as Kohlrausch's method, and consists of the simple Wheatstone bridge arrangement, with a telephone-receiver in the place of a galvanometer, and the alternating current from the secondary of a small induction-coil instead of a simple battery of cells. With this arrangement the alternating current produces a humming sound in the telephone when the bridge is out of balance. The alternating current in addition does not decompose the electrolyte, and allows of conductivity determinations being made with great accuracy. Having described the apparatus, some of the results will now be given. The first experiments were made with an electrolyte consisting of dilute sulphuric acid in the proportion of 10 cubic centimeters of H_2SO_4, specific gravity 1.84664, in 40 cubic centimeters of distilled water, and

a wire of German silver made equal in resistance by means of a rheostat of the *non-inductive type*. This is an important point to
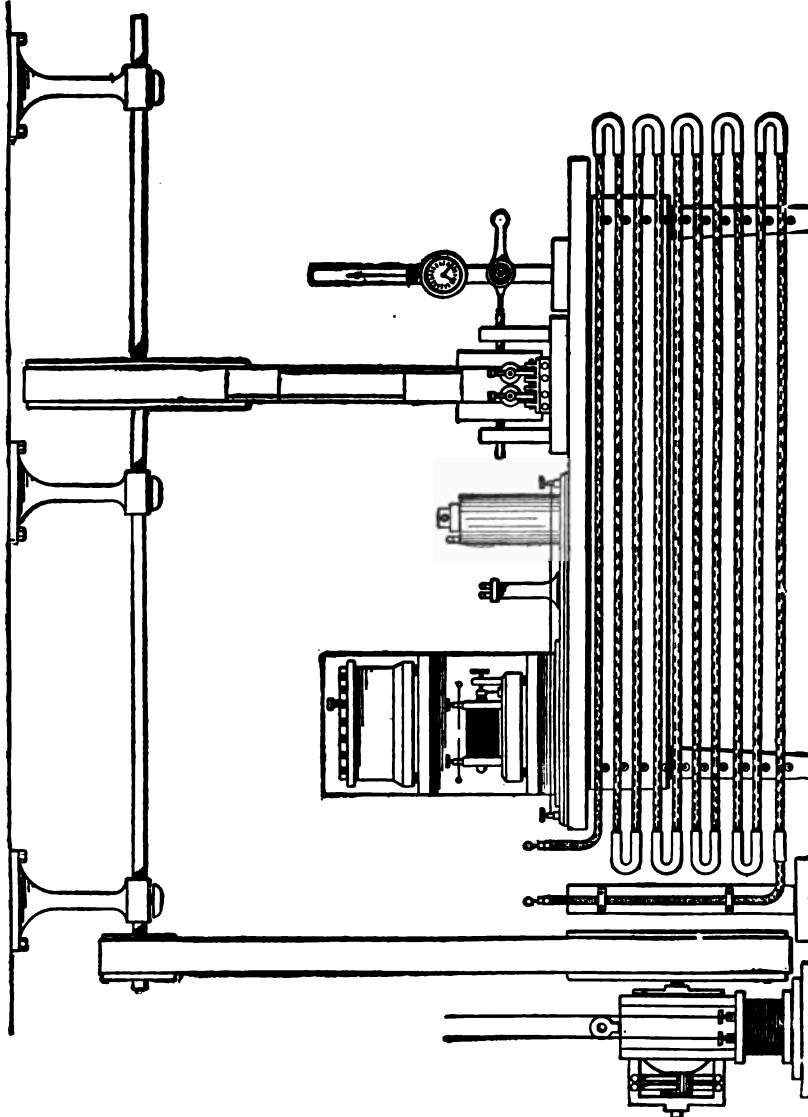
Fig. 36.—Special High-speed Electrochronograph Capable of Dividing a Second into a Million Parts in Connection with Fifty Feet of Electrolyte for Studying Velocity of Electrolytic Conduction. This chronograph is driven by a 2 H.P motor, as shown at the left, belted up for multiplication of speed.

observe in determining all resistances where only a momentary current is to be dealt with. For a dissertation upon the subject of

non-inductive resistances, the student must be referred to any standard work on physics dealing with electrical measurements. The present writer may say, however, that with common coil resistances, or rheostats, there is a choking or damping effect upon electrical impulses of short duration, due to the phenomenon of self-induction.   Having balanced the respective resistances of the electrolyte and wire with its *non-inductive resistance* rheostat in series, the chronograph was speeded up, and when a rate of 2000 revolutions per minute was reached, as counted by the revolution-counter upon the *drum-wheel shaft*, the key was closed three times in rapid succession and the chronograph stopped. Three records had been made. At first it was found that the electromagnet in series with the electrolyte struck a trifle in advance of the electromagnet in series with the wire, the marking on the band leading by 0.75 centimeter, indicating that the conductivity through the electrolyte was ahead by 1/10,000 of a second. What was this due to? Although the two resistances were balanced as carefully as possible, the leading of the electrolyte was undoubtedly due to the fact that its resistance was slightly lower than that of the wire. The resistances were carefully rebalanced, using the most refined means, when the two conductors finally "struck abreast," so to speak, upon the flying band.   Electrolytes of various composition were substituted for the sulphuric acid and carefully compared with the wire, and in every case where the resistances had been perfectly balanced the two electromagnets struck abreast. The highest speeds of bands were of course obtained with the large instrument as shown in Fig. 36, and with this equipment, electrolytes of various lengths were experimented with. An electrolyte 50 feet in length conducted as quickly as an electrolyte only a few centimeters long. It mattered not whether we used an electrolyte with light or heavy ions, the rate of conductivity, or response to the electric current, was the same. Experiments were also conducted with storage-batteries as a source of electricity, and it was recorded here again that the electricity left the free ions in the storage-cells as readily as it did a wire charged by a dynamo current. Experiments of this character were repeated many times, and the writer believes one is justified in stating the law that *electrolytes of equal resistance conduct the electric current with a definite velocity regardless of the composition of the electrolytes or the*

length of the containing vessel. It may also be stated that *an electrolyte conducts the electric current as quickly as a conductor of the first class, regardless of its composition, provided we have an equal ohmic resistance of a non-inductive type.* In working with fused electrolytes the same quantitative behavior was observed, the electric current flowing as quickly after contact as with all metallic conductors. Free ions must therefore be around the electrodes and in contact with them. If molecules had to be first broken down into ions, and these ions had to travel, there would undoubtedly be a lag in experimenting with electrolytes consisting of heavy ions, for the question of inertia would be involved. The same impulse which would start up light ions in a given time would fail to produce the same response where heavier ions were concerned. Having shown the instantaneous behavior of electrolytes toward the electric current, we are now in a position to study the experimental methods for measuring the absolute velocity of ions.

Experimental Methods for Showing the Absolute Velocity of Ions. Lodge's Apparatus.

It has been stated that all ions had their respective velocities, and that these velocities were exceedingly small. It has been demonstrated by Bredig, and also by Ostwald, that the velocity or mechanical motion of the ions is a function of their atomic weights. This relationship was brought out by series of long and patient research, but the reason for such behavior is not understood. We have in chemistry several striking cases of periodic behavior, although we have so far been unable to account for them. If we arranged the ions in a table according to their migration rates, we would find that hydrogen is the swiftest of them all, although its movement through an electrolyte requires considerable time. Let us look into the method of Lodge, and learn just what the speed of the hydrogen ion is. Fig. 37 illustrates the apparatus of this physicist for determining the speed of the hydrogen ion under a given potential gradient. Here we have two beakers or glass jars joined by a siphon-tube bent at right angles at each end. A centimeter-scale is attached to the under side of this tube as indicated. This glass siphon-tube contains an aqueous solution of gelatine put in hot, which solidifies when

cold, forming a jelly. Now this solution of gelatine also contains some sodium chloride, NaCl, to serve as the electrolyte, and the entire solution is colored red by the addition of a little phenolphthalein made alkaline with a few drops of sodium-hydroxide solution. The gelatine is dissolved in hot water in a beaker and some common salt is added and stirred until a perfectly homogeneous solution is obtained. A little phenolphthalein is then stirred in and made red by adding a few drops of the sodium-hydroxide solution. This mixture is kept near the boiling-point of water for a few minutes, and is then poured into a number of tubes bent at
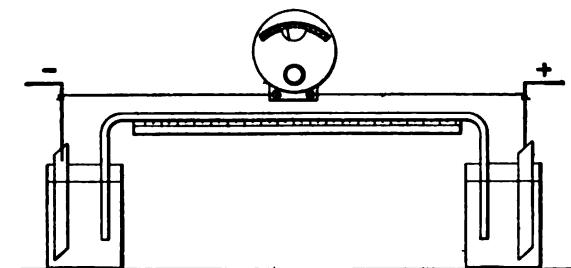
FIG. 37.—Lodge's Apparatus for Experimentally Determining the Absolute Velocity of the Hydrogen Ion.

right angles to form siphons like that illustrated. Care must be taken to avoid the inclosing of air-bubbles, and the tubes are put away to cool and solidify with the bent ends turned up. To measure the velocity of the hydrogen ion, one of the tubes after cooling is placed ·dipping into the two beakers as shown, and the beakers filled with a dilute solution of sulphuric acid. Two platinum electrodes are put in place and connected to our motor-generator or lamp-bank, with a voltmeter joined across the electrodes to show the potential gradient under which we are working. All ions have a fixed velocity under a set potential gradient. Now, what takes place when a current of electricity is made to pass through this system? The hydrogen ion from the electrolyte of sulphuric acid starts from the anode in the right-hand beaker and makes its way to the cathode in the left-hand beaker through the composition in the siphon-tube. What happens there? The hydrogen simply displaces the sodium from the sodium chloride present and forms hydrochloric acid, $H + NaCl = HCl$, which decolorizes the gelatinous solution of phenolphthalein.

This indicator is red in the presence of a base and colorless in the presence of an acid. As the hydrogen ion proceeds through the siphon-tube, it replaces the sodium in the sodium chloride, and bleaches out the phenolphthalein marking its way through the composition. The experiment is an interesting one to watch, as the decoloration proceeds at a slow rate. Lodge worked with a potential gradient equivalent to a drop of one volt a centimeter. If we have a tube 50 centimeters long, therefore we must use a difference in potential of 50 volts, and must employ our lamp-bank for this, unless we have at hand a dynamo wound for a current output at 50 volts. For a short tube we can use our motor-generator. Working with such a piece of apparatus with a drop of one volt per centimeter, Lodge found the absolute velocity of the hydrogen ion to be about $1\frac{2}{3}$ centimeters per minute. In three determinations Lodge found the hydrogen ion to travel:

<div align="center">

1.1560 centimeters per minute.

1.1740   "   "   "

1.1440   "   "   "

</div>

The average of these three determinations with the above apparatus being 1.1580 centimeters per minute, or considerably over an hour for this, the swiftest of all ions, to travel a meter; and yet as shown by the electrochronograph work, an electric current leaps through an electrolyte, so to speak, in exactly the same time as it does through a wire.

Whetham's Method.

Another experimental method for determining the absolute velocities of ions was devised and used by Whetham, the apparatus being illustrated in Fig. 38. He describes his method as follows: "Suppose we have two solutions like copper chloride and ammonium chloride, containing one ion in common and having nearly equal conductivities. Let one solution be colored and have a density different from that of the other. The denser solution is first poured into the longer arm of a kind of U tube, and then the other is allowed to flow gently on to its surface from the shorter arm. If a current is passed across the junction between the two solutions, it carries the copper and ammonium ions with it and drives the chlorine ions in

the opposite direction.   Since the color depends on the presence of
the copper ions, the boundary will travel with the current, and by
measuring its velocity the speed of the
ions under unit potential gradient can
be calculated." There are several other
methods for determining absolute veloci-
ties of ions, and in the hands of careful
investigators the results agree very strik
ingly.   As will be seen later, there are
methods for determining the relative
velocities of the ions, and it will be seen
at once if we have the absolute velocity
of one ion accurately determined, and
we can ascertain in other ways the rela-
tive velocities of the remaining ions, we
can calculate the absolute velocities of
them all.   Having learned about electro-
lytes, dissociation, ionic velocity, etc., we
will be in a good position to take up
and appreciate work of a little more
practical character in our next chapter,
and introduce the student to the beauti-
ful work of Faraday in electrochemical

Fig. 38.—Whetham's Appara-
tus for Experimentally Deter-
mining the Absolute Veloci-
ties of Ions.

science.   Here we will study the quantitative relation of the electric
current to electrolytes, and take up the energy relations between
chemistry and electricity, and lay the foundation for work of a very
practical and useful character.

CHAPTER VI.

FARADAY'S LAW.

DISTINCTION BETWEEN CURRENT REQUIRED AND ENERGY ABSORBED. EXPERIMENTS TO SHOW MECHANICAL MOVEMENT OF MATERIAL.

THE idea occurred to Faraday to send a current through several electrolytes connected up in series, and to make weighed comparisons of the materials separated by the same current in a given time. In 1883, the result of Faraday's most important and valuable work was framed into the following law by H. Von Helmholtz:

"*The same quantity of electricity passing through an electrolyte either sets free or transfers to other combinations always the same number of valencies.*"

Von Helmholtz, in his "Faraday lecture" delivered in London, on April 5, 1881, laid the foundation of a new electrochemical theory which explains the facts embraced by Faraday's law. The most important of these facts may be stated in this sentence:

"*Every single valency of an elementary or compound ion is charged with exactly the same quantity of positive or negative electricity, which behaves as if it were an electrical atom that cannot be further divided.*"

As the work of Faraday is of such great moment in theoretical and practical electrochemistry, the actual words of Von Helmholtz are given, the author believing that the facts as learned by Faraday are among the first, if not the most important, of all here recorded. The words used by Von Helmholtz are these, as translated by M. M. Patterson Muir:

"*The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion, and accompanies it during all its motions through the interior of the electrolytic fluid.*"

"*This quantity we may call the electric charge of the atom.*

"*If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long at it moves about in the electrolytic fluid, each ion remains united with its electric equivalent or equivalents.*

"*At the surface of the electrodes decomposition can take place if there is a sufficient electromotive force, and then the ions give off their electric charges and become electrically neutral.*"

From this work the valuable table of *electrochemical equivalents* was compiled, which is of the utmost importance in all practical electrochemical work. The definition of an electrochemical equivalent being capable of expression in several ways, it should be carefully studied and appreciated. If the quantities of all ions which stand to one another in the relations of their combining weights carry equal quantities of electricity, it will at once be appreciated that it is of great scientific importance to know the exact amount of electricity which a unit quantity of ions will carry. This can be determined by passing a given quantity of electricity through a solution of an electrolyte and weighing the amount of metal deposited upon the cathode, or measuring the amount of gas liberated and calculating its weight from its volume. This has been done very carefully by Lord Rayleigh and Mrs. Sedgewick, who found that one coulomb of electricity deposits 1.1179 milligrams of silver. W. and F. Kohlrausch, working with equal care, found under the same conditions 1.1183 milligrams. The mean of these figures is 1.1181 milligrams. A more recent determination of the electrochemical equivalent of silver by Richards, Collins, and Heimrod gives 1.1172 milligrams of silver as equivalent to one coulomb. A still more recent determination by Patterson and Guthe gives the slightly larger value of 1.1192 milligrams as equivalent to one coulomb. This agrees with the mean result obtained by Pellat and Portier, and is very close to the number obtained by Kahle, 1.1193. The mass of the ions taken is purely arbitrary. Here, as in so many other cases, it is convenient to use the gram-molecular weight for univalent and the gram-equivalent weight for polyvalent ions. For all practical purposes

the electrochemical equivalent of silver, which is usually referred to as a standard for determining the other values for the other elements, is set down as the fraction of a gram as equivalent to one coulomb, thus: 0.0011193 gram.   The atomic weight of silver in terms of oxygen = 16 is 107.93.   In order to separate a gram-atomic weight of silver it will require, using W. and F. Kohlrausch's mean of .0011181,

$$\frac{107.93}{0.0011181} = 96{,}530 \text{ coulombs of electricity.}$$

This number of coulombs, 96,530, as will be seen, will separate the gram-atomic weight of any univalent body, and is sometimes called the *electrochemical equivalent of electricity*.   The fact may be stated thus:

One chemical equivalent of any electrolyte expressed in grams requires the passage of 96,530 coulombs for its liberation or electrolysis; 96,530 coulombs, therefore, are capable of liberating the chemical equivalent of any electrolyte.

This is an exceedingly important *constant* for us to remember in our practical work.   This number varies in value a trifle according to different investigators, and will be encountered as 96,540, etc.   In the table opposite the chemical equivalents of some of the most important elements are given.   The student must not confound a chemical equivalent with an electrochemical equivalent. These terms must be clearly separated in his mind or else he will be continually getting into confusion.   A chemical equivalent is simply the atomic weight of a substance divided by its valence.   The atomic weight of oxygen being 16, and its valence 2, the chemical equivalent of oxygen would be 8.   Oxygen = 16.   Chemical equivalent 16 ÷ 2 = 8.

In the table on page 84 the *electrochemical equivalents* of some of the most important elements are given.   By dividing the atomic weight in the second column by the valence in the third column, the chemical equivalent given in the fourth column is obtained, and this number multiplied by the electrochemical equivalent of hydrogen in micrograms per coulomb gives the electrochemical equivalent of the ion in the fifth column, also in micrograms per coulomb.   The numbers in the sixth column are the reciprocals of

CHEMICAL EQUIVALENTS OF CERTAIN ELEMENTS.

Element.	A. W.	C. E.	Element.	A. W.	C. E.
Al'''	$\dfrac{27.1}{3\ \text{valence}}$	9.03	Pb''	$\dfrac{206.9}{2\ \text{valence}}$	103.45
Ba''	$\dfrac{137.4}{2}$	67.8	Li	$\dfrac{7.03}{1}$	7.03
Br.	$\dfrac{79.96}{1}$	79.96	Mg''	$\dfrac{24.36}{2}$	12.18
Cd''	$\dfrac{112.4}{2}$	56.2	Mn''	$\dfrac{55}{2}$	27.5
Ca''	$\dfrac{40.1}{2}$	20.05	Hg	$\dfrac{203.3}{1}$	203.3
Cl	$\dfrac{35.45}{1}$	35.45	Hg''	$\dfrac{203.3}{2}$	100.15
Cr''	$\dfrac{52.1}{2}$	26.05	N'''	$\dfrac{14.01}{3}$	4.67
Cu.	$\dfrac{63.6}{1}$	63.6	Ni''	$\dfrac{58.7}{2}$	29.35
Cu''	$\dfrac{63.6}{2}$	31.8	O''	$\dfrac{16}{2}$	8.00
F.	$\dfrac{19}{1}$	19.00	K	$\dfrac{39.15}{1}$	39.15
Au.	$\dfrac{197.2}{3}$	65.73	Ag	$\dfrac{107.93}{1}$	107.93
H.	$\dfrac{1.008}{1}$	1.008	Na	$\dfrac{23.05}{1}$	23.05
I.	$\dfrac{126.85}{1}$	126.85	Sn''''	$\dfrac{119}{4}$	26.75
Fe''	$\dfrac{55.9}{2}$	27.95	Sr''	$\dfrac{87.6}{2}$	43.8
Fe'''	$\dfrac{55.9}{3}$	18.63	Zn''	$\dfrac{65.4}{2}$	32.7

those in the fifth given in grams. The electrochem'cal equivalents of compound ions, such, for example, as the univalent radical hydroxile OH and the bivalent radical SO_4, are similarly obtained, the chemical equivalent of such a radical being the sum of its comp nent atomic masses div ded by its valence.

This table brings out the beautiful tru h of Faraday's law, and forcibly indicates the great value of the facts he was able to point out as a result of his famous investigations. Let us experimentally test Faraday's law in the laboratory and put down our results. For this purpose we will set up a piece of apparatus with five different

electrolytes in series and weigh the cathode products liberated by the same current-flow.

TABLE SHOWING RELATIVE WEIGHTS OF BODIES LIBERATED BY A COMMON ELECTRIC CURRENT.

Element.	Atomic Mass.	Valence.	Chemical Equivalent.	Electrochemical Equivalents	
				Micrograms per Coulomb.	Coulombs per Gram.
1st	2d	3d	4th	5th	6th
Hydrogen............	1	1	1	10.38	96,340
Oxygen.............	15.96	2	7.98	82.83	12,070
Chlorine...........	35.37	1	35.37	367.10	2,724
Nitrogen...........	14.01	3	4.67	48.47	20,630
Aluminium.........	27.04	3	9.01	93.50	10,700
Lead...............	206.40	2	103.20	1071.00	933.7
Zinc..............	64.88	2	32.44	336.70	2,970
Nickel............	58.60	2	39.30	304.20	3,287
Mercury...........	199.80	2	99.90	1037.00	964.3
Mercury...........	199.80	1	199.80	2074.00	482.2
Copper............	63.18	2	31.59	327.90	3,050
Copper............	63.18	1	63.18	655.80	1,525
Silver............	107.70	1	107.70	1118.00	894.5
Gold.............	196.2	3	65.40	678.90	1,473

EXPERIMENTAL DEMONSTRATION OF FARADAY'S LAW.

Referring to Fig. 39, we have at the left a Hoffmann apparatus, A, for the electrolysis of solutions yielding gaseous products at the electrodes. The gases libe ated es ape into the two tubes and press the solution up into the reservoir by the central tube. By opening the stopcocks at the tops of the two side tubes containing the gases, the weight of the solution in the reservoir will force the gases out, when they may be collected in a most convenient manner. Hydrogen, for example, may be burned as a jet, after electrolyzing a dilute solution of sulphuric acid, or as we learned in the first chapter, by electrolyzing a solution of potassium or sodium hydroxide. Oxygen and hydrogen will be liberated in such a piece of apparatus in the ratio of two volumes of hydrogen to one volume of oxygen whether we use dilute ulphuric acid, or a sodium, or potassium-hydroxide solution. For the present demonstration of the law of Faraday, we will fill the Hoffmann apparatus with a dilute solution of sulphuric acid in distilled water in the propor-

tion of about 1 to 10. In the cell B we will place a concentrated neutral solution of silver nitrate in distilled water. In the cell C we will place a solution of *cuprous* chloride, which may be made by dissolving a few grams of the salt in hydrochloric acid after having washed it carefully on a filter paper with warm distilled water. In the cell D we will place an electrolyte consisting of copper sulphate slightly acidulated with nitric acid. In the cell E we will use a solution of *stannic* chloride, best prepared in the fol-
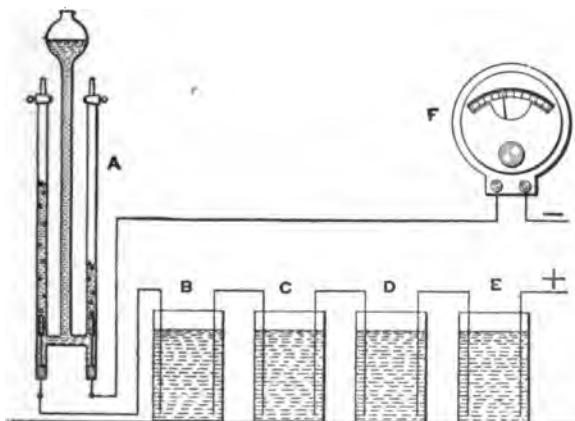

FIG. 39.—Simple Apparatus for Experimentally Demonstrating Faraday's Law. *A*, Hoffmann apparatus; *B, C, D,* and *E,* cells containing electrolytes and electrodes; *F,* delicate ammeter.

lowing manner: Take of stannous-chloride crystals 1000 grams; hydrochloric acid, specific gravity 1.125, 1170 cubic centimeters; nitric acid, specific gravity 1.220, 435 cubic centimeters; and distilled water 1000 cubic centimeters. Put the stannous chloride into a 12-inch evaporating-dish and add the 1170 cubic centimeters of hydrochloric acid; warm on the steam-bath and stir until the salt is dissolved; then dilute with one liter of hot water. If the solution does not remain clear, there is a deficiency of hydrochloric acid, in which case add very concentrated hydrochloric acid, a few drops at a time, until the solution becomes clear. Add the nitric acid, a few cubic centimeters at a time, to the warm solution, stirring well after each addition. After a considerable part of the nitric acid has been added, test a few drops of the solution with a drop of mercuric-chloride solution. If a white precipitate falls,

stannous chloride is present, and more nitric acid is needed. **When**
no white precipitate falls, the oxidation is complete, and no more
nitric acid should be added. Put the liquid product into a **tightly**
stoppered bottle. The cathodes of all the cells are to be of
platinum, but we must have a silver anode in the silver-nitrate
solution and copper anodes in both of the copper solutions. The
anode in the tin solution may be of platinum. It is needless
to say that both of the electrodes in the Hoffmann apparatus are
of platinum. These five electrolytes are now all connected in series
with a delicate ammeter, as shown, and the terminal wires run to
a storage-battery or such a motor-generator as described in the
first chapter. The electrolysis may be allowed to proceed for any
length of time within the capacity of the Hoffmann apparatus.
The longer the run the better, the errors in weighing a decided
increase in the respective cathodes being less than in weighing a
slight increase. In this system we will have hydrogen liberated,
the monovalent element silver, the monovalent copper, the divalent
copper, and the tetravalent tin. If the experiment has been
conducted without error and losses, we will have for each gram of
hydrogen liberated 107.93 grams of silver, 63.6 grams of copper
in our monovalent copper electrolyte, 31.8 grams of copper in our
divalent copper solution, and 26.75 gramms of tin from the tin
solution. The following table shows the result of a carefully con-
ducted experiment with the five electrolytes described above:

Weight of deposit re- ferred to 1 g. H.....	108.3 g. Ag′.	63.5 g. Cu′.	31.45 g. Cu″.	28.29 g. Sn‴‴.
Atomic weight.......	107.93	63.6	63.6	119.00

Here we can see that the monovalent elements separate in pro-
portion to their atomic masses, the divalent elements in propor-
tion to their atomic masses divided by two, the tetravalent element
in proportion to its atomic mass divided by four. The beauty of
this law is very striking, and it may be said that Faraday's law
knows no exceptions. There can be no electrolytic conduction
without the corresponding setting free of substances in the ratios of
their chemical equivalents. As we shall see presently, we have
ample proof of moving particles, or an actual mechanical transfer
of matter when an electric current is passed through an electrolyte.
In view of the mechanical transfer of matter, experiments were con-

ducted upon electrolytes under heavy pressure to learn if Faraday's law held true under such conditions. At first it was noted that the electrical conductivity was *increased*. In other words, more current passed through the electrolyte than was accounted for by weighing the cathodes. As a matter of fact the method of conducting the experiment was faulty. The pressure was put upon the electrolyte by air, some of which was of course forced into solution, and ionizing carried a *portion of the electric current*. Professors Nernst and Ostwald, in Germany, tested Faraday's law most critically by electrolyzing solutions with exceedingly feeble currents to see if any electricity at all was conducted without corresponding quantitative decomposition of the electrolyte. In one experiment upon dilute sulphuric acid they caused an exceedingly small amount of electricity to pass—only 0.000005 coulomb. They determined the minute quantity of gas set free and found that Faraday's law held even for such a small electric current. In the large commercial electrolytic copper refineries the law has been tested upon enormous scales by the passage of millions of coulombs and found to hold absolutely. The law of Faraday in the light of the many attacks and investigations upon it seems to be one of the very few in chemical and physical science which have stood throughout without suffering exception of any kind. We have now learned that *chemical equivalent quantities of all ions have the same capacity for electricity*. It is a striking and interesting fact to note that this is analogous to the law of Dulong and Petit, which states that *all atoms have the same capacity for heat*. If we multiply the atomic weights of the elements by their specific heats we obtain almost a constant, which number we term *atomic heat*. The following table containing a few elements for the purpose of illustration is of interest here.

Element.	A., Atomic Weight.	S., Specific Heat.	A. × S., Atomic Heat.
Potassium.	39	.166	6.5
Calcium.	40	.170	6.8
Manganese.	55	.122	6.7
Tin.	118	.054	6.5
Gold.	197	.032	6.3
Mercury.	200	.032	6.4
Lead.	207	.031	6.4
Bismuth.	209	.030	6.3
Silver.	108	.056	6.0

To this law there are some exceptions, but in the majority of cases we have practically a constant.

VOLTAMETERS.

METAL AND GAS TYPE. THE SILVER VOLTAMETER.

The most accurate instrument for measuring current-flow is without question the silver voltameter, and is at the same time the most easily constructed.

Fig. 40 will make the arrangement clear. Two comparatively heavy plates of pure silver are joined together to make one electrode, between which a thin silver sheet forming the other electrode is suspended. In the silver voltameter the very high equivalent of
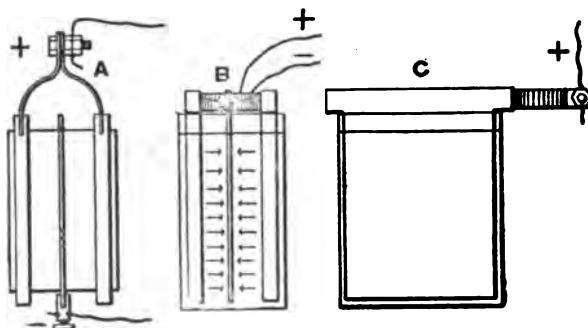
FIG. 40.—Construction of Silver Voltameter for the Measurement of Current-flow in Coulombs. *A*, top view looking down into cell; *B*, end view; *C*, side view.

silver, and consequently the great mass isolated upon the cathode by comparatively feeble currents, reduce the errors in weighing to a minimum. There is one disadvantage in the use of the silver voltameter, however, and this is due to the fact that silver tends to precipitate out upon the cathode in crystalline form, and if the electrolyzing current is strong, some of the crystals form so quickly that they will drop off and introduce errors from this cause. The electrolyte for this instrument is of a concentrated neutral silver-nitrate solution. With such an instrument a current of one ampere deposits upon the thin silver cathode

> 0.0011181 gram silver per second,

or 0.067086 gram silver per minute,

or 4.025160 grams silver per hour.

With such an instrument in series with an electric current, by determining the weight of the cathode before and after the run we are in a position to calculate the number of coulombs that have passed through the system. If we had an absolutely steady current we could get at the same thing by putting a correct ammeter in series and multiplying the amperes indicated by the number of seconds during which the current passed and get the coulombs used. If the strength of the current varied, however, this plan would be worthless. With voltameters of either the metal or gas type the current may vary, flowing at very different rates in a given time, but the increase in weight of the cathode will give the true number of coulombs regardless of such fluctuations.

THE COPPER VOLTAMETER.

Here we have a similar construction, only with plates of pure copper instead of silver ones. The electrolyte consists of a solution of 30 grams of crystallized chemically pure copper sulphate dissolved in 200 grams of distilled water, to which 5 grams of chemically pure concentrated sulphuric acid is added and 5 cubic centimeters of ethyl alcohol. Such an instrument is inexpensive and is adapted to the most general requirements. The copper voltameter can be left in circuit with work through great lengths of time without fear of losing any copper by falling from the cathode. The copper will be deposited upon the cathode as a beautiful, salmon-pink metal. Such an instrument will answer every purpose as an ampere-hour meter for heavy work if the plates are made generous enough in area. With this voltameter a current of one ampere deposits upon the thin copper cathode

0.00033 gram of copper per second,

or   0.01980 gram of copper per minute,

or   1.18800 grams of copper per hour.

This will be found the most satisfactory instrument for general work and every student in practical electrochemistry should set one up for his current measurements. With very small currents, however, there is apt to be a slight error introduced with the use of the copper voltameter because of some cuprous oxide being deposited

along with the copper. If we have at least 0.1 of an ampere following through the instrument, and its cathode area is at least 100 square centimeters, there will be no trouble from this cause, especially when the electrolyte contains the sulphuric acid and alcohol as given in the above formula.

THE GAS-VOLTAMETER.

In this instrument either dilute sulphuric acid or a solution of potassium or sodium hydroxide may be used and the mixed oxygen and hydrogen gases determined by volume. Dilute sulphuric acid is perhaps the best for the purpose, and should be mixed in the proportion of one part of strong sulphuric acid to ten or twelve parts of distilled water. The acidulated water is decomposed between two platinum plates and gas collected and reduced to 0° and 760 millimeters by the well-known formula for reducing gases to a standard for comparison. This type of voltameter, as illustrated in Fig. 41, is very convenient because it does
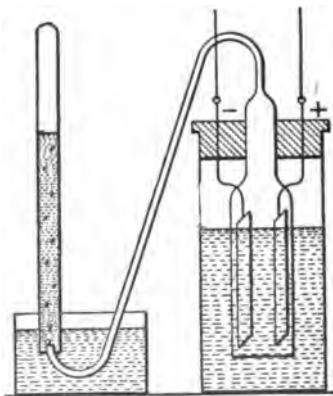
FIG. 41.—Approved Form of Gas Voltameter for the Measurement of Current-flow in Coulombs. The student must not confound the word voltameter with the word voltmeter.

away with all weighings. The volume can be read, and by means of tables, when the temperature has been taken, the gas volume can be quickly reduced to a standard. This instrument is not quite as accurate as the copper voltameter, and, moreover, requires about two volts of electrical pressure to drive a current through it. If we are using a storage-battery or the motor-generator we

must take into consideration the two volts required by such a volt-
ameter in making any calculations. To use the voltameter the water
in the vertical measuring-tube should first be saturated with oxy-
hydrogen gas, by allowing it to fill about half full, and then discon-
necting and shaking, with the thumb or a stopper closing the end of
the tube. With this type of instrument an ampere flowing liberates

<blockquote>
0.1740 cc. of oxyhydrogen gas per second,
</blockquote>

or   10.4400 cc. of oxyhydrogen gas per minute,

or   626.4000 cc. of oxyhydrogen gas per hour.

The above volumes are at 0° and 760 millimeters pressure. The
vertical tube for collecting the gas is best graduated direct into cubic
centimeters, reading to tenths. Such a gas-voltameter must be
ordered from one of the chemical supply houses unless the student
is an expert glass-blower, but one answering every requirement can
be quickly made in the laboratory without the art of glass-blowing,
as illustrated at *A* in Fig. 42. Here we have a glass cylinder fitted
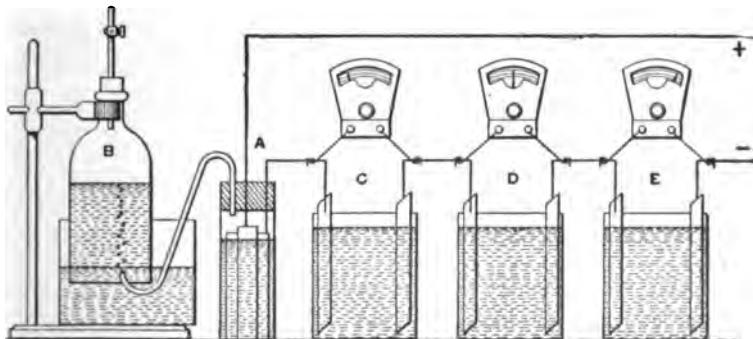
FIG. 42.—Gas-voltameter and Large Collecting-jar in Series with Three Electrolytic
Cells equipped with Voltmeters. *A*, easily constructed gas-voltameter; *B*, col-
lecting-jar; *C*, *D*, and *E*, electrolytic cells with voltmeters for determining the
electrical energy expended in each electrolyte.

with a tight stopper (the whole success of the apparatus depends
upon its being tight), containing two concentric platinum cylinders,
one forming the anode and the other the cathode. The large bell
jar, *B*, allows of a long run before it is necessary to stop and measure
the gas volume. The bell jar may be graduated and its readings
taken for rough work, but for close work the gas must be transferred
to a more delicate graduate and reduced to standard conditions.

Now we have just learned that the same current will deposit upon the cathodes of electrolytic cells in series chemical equivalents of the elements as well as chemical equivalents of compound ions. Chemical equivalents of all bodies are therefore liberated or deposited by the same current. Is the *absorption of energy* the same in these different cases? It is not, and the experiment illustrated in Fig. 42 has been designed by the writer to bring out this most important point. Let us place three different electrolytes in the cells C, D, and E, and connect across the electrodes in each case a delicate voltmeter to indicate the fall of potential in each cell. Although the coulombs passed will of course be equal in each cell, because they are in series, and the metals will be deposited in the ratio of their chemical equivalents, the number of joules expended in each cell will be different. Those who have studied electricity will know that the joule is the unit of electrical *energy*, and is the product of the ampere by the second, by the volt. As a coulomb is the product of an ampere by a second, we may say that the joule is the product of a coulomb by a volt. It is not the intention of the author to go into the reason for unequal absorptions of energy in different electrolytes until the next chapter, when the matter will be fully dealt with. It is, however, the wish of the writer to impress upon the student *that there is a difference*, and that its explanation, as will be learned later, is in accordance with the doctrine of conservation of energy, and a point of great beauty in electrochemistry. With an arrangement of apparatus as indicated in Fig. 42, therefore, we would be able to calculate by means of the gas-voltameter in series, the number of coulombs which have passed through the system, and by the respective readings of the voltmeters across the electrodes of the respective cells we would be able to determine the amount of energy absorbed in each. So much upon this point for the present. It was stated that we should have introduced in connection with Faraday's law, experimental evidence proving that the passage of an electric current through an electrolyte was accompanied by an actual mechanical transfer of matter. A very simple and a very beautiful experiment may be quickly performed which goes to show the transport of ponderable material. Arrange a large U tube, as illustrated in Fig. 43, with stoppers and platinum electrodes. Through one stopper bore a small hole to receive a bent glass tube as shown.

Prepare a concentrated solution of zinc chloride in distilled water to serve as the electrolyte. Arrange the tube in series with the lamp-bank and electric-lighting circuit as described in Chapter I, and throw in one or two lamps. The zinc will immediately begin to grow in the form of a beautiful metallic tree and chlorine may be detected issuing from the bent glass tube over the opposite pole. There is optical evidence that we have an accumulation of metal at the cathode, and evidence of an equally striking nature that we have chlorine at the anode. In the drawing, the bleaching action is shown upon a piece of calico. What is taking place at the bend in the bottom of the tube, however? Have we mechanical movement there? We have been led to believe that we have chlorine ions moving in one direction and zinc ions moving in the other. ‧ Is it true, and is there any experiment to prove it? The author has designed three to furnish evidence in support of this, and they are here published for the first time in book form. The first of the three experiments is illustrated in Fig. 44. Although glass is always stated to be the best electrical insulator known, it occurred to the writer that its constituents could carry the electric current if the ions were only free to migrate. In other words, glass was regarded by the writer as being a *solid electrolyte.* Ordinary glass, as is well known to the general chemist, consists of silicon dioxide fused with calcium and sodium carbonate. Ordinary glass is therefore a soda lime, silicon-dioxide glass. Bohemian glass is made with potassium carbonate, and flint glass is made by melting together lead oxide, potassium carbonate, and silicon dioxide, while strass is a species of glass very rich in lead. We have, as may be seen, all the ions necessary to carry electric currents if they were only free to move about. To test this point little rods of solid glass of the different varieties were softened and platinum wires run into the ends to a distance of about a centimeter. The rods were cut about 3 centimeters long, so there was in each case an "insulating gap" of about a centimeter between the ends of the platinum
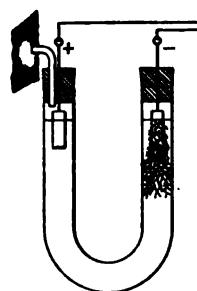
Mechanical Transport of Matter.

FIG. 43.—Electrolysis of a Solution of Chloride of Zinc, showing the rapid growth of a "zinc-tree" and the liberation of chlorine as indicated by its bleaching action.

wires. A glance at the figure shows such a glass rod with the plati-
num wires at *B*. A delicate milliammeter is joined in series with the
platinum wires and our lamp-bank (not shown in the illustration),
and of course no deflection is shown upon the indicating instrument
because glass is an insulator when cold. Now bring a Bunsen
burner, *A*, under the glass rod and heat it up gradually. As the
glass begins to soften and flow, *the milliammeter begins to show con-
ductivity.* With the softening of the glass, therefore, the *ions are free
to travel.* This is a very pretty and convincing experiment when
performed with a large-scale ammeter so that in a lecture-room an
entire class may see the deflection of the needle. It is of interest
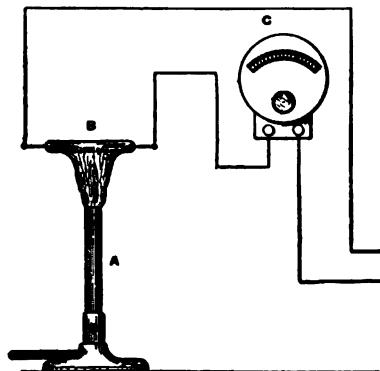
FIG. 44.—Simple and Easily Performed Experiment to Show Mechanical Transfer
of Matter through Solid Glass. *A*, Bunsen burner; *B*, solid rod of glass; *C*,
milliammeter to show conduction of the electric current.

at this time to point out the fact that all electrolytes when in solution
in water conduct better when heated up. This is just the reverse
with metals and alloys.

EXPERIMENTS WITH FROZEN ELECTROLYTES.

What will be the effect upon the movement of ions on freezing an
electrolyte? This question presented itself to the writer, and not
coming across records of any experiments with frozen electrolytes,
or any theoretical discussion of the same, it was decided to investigate
the matter experimentally. According to our ionic migration, or
convection theory of electricity through substances in solution, the
conductivity of an electrolyte should cease or approach zero value

when frozen. When the medium containing the ions is frozen solid will the conductivity actually cease? Will the ions move freely through as before, or can they be forced through at diminished velocity? The writer has made numerous experiments upon the physical properties of ice, and has found it to be viscous-like in behavior. This property has also been demonstrated by Professors Tyndall and Agassiz upon a tremendous scale in their studies of the Swiss glaciers. Ice can be bent, twisted, and pressed into molds, and be made to flow under pressure like semi-molten glass. The ions in a frozen electrolyte, therefore, should be in a measure free to move slowly when subjected to an electric current. Let us look into the facts of actual experiments. Fig. 45 shows a
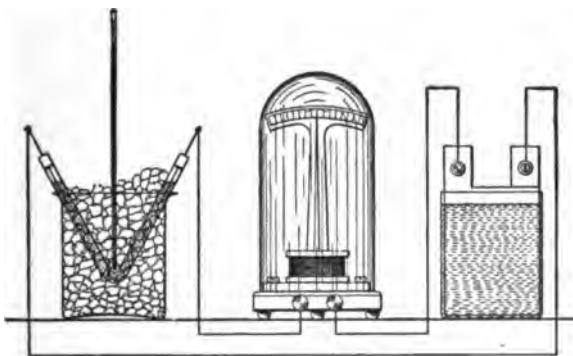
FIG. 45.—Experiment with Frozen Electrolytes. The "V" tube at the left of the drawing contains the solution to be frozen and is immersed in a beaker containing the freezing-mixture. Indicating galvanometer in the center, storage-battery at right. Three cells of battery at least are necessary in this experiment or else the lamp-bank shown in Chapter I.

simple arrangement for experimenting with frozen electrolytes. The following experimental work embraced the freezing of a dozen or more solutions, including NaCl, KCl, HCl, H_2SO_4, $K_2Cr_2O_7$, KI, etc., and in every instance, with an ordinary ammeter in series, the current *appeared to be completely stopped* when the solvent containing the ions was solidified. The temperature in each case was well below the freezing-point, the solutions frozen being very dilute not only for the sake of complete dissociation of the salts, but for the comparative ease with which they could be frozen. The freezing-mixtures consisted of pounded ice and salt and also the well-known

mixture of sodium sulphate 6 parts, ammonium nitrate 5 parts, dilute nitric acid 5 parts. The lowest temperature attained by the use of this mixture was $-30°$ C., which was more than ample to freeze any of the above dilute solutions. The plan of conducting an experiment which is suitable for a lecture-room experiment is shown in the illustration and consists of a V tube of glass fitted with stoppers and platinum electrodes, which may be immersed in the beaker containing the freezing-mixture. A large upright galvanometer is shown in the center and a cell of storage battery at the right. One cell of battery is rarely sufficient for electrolysis, as will be learned in the next chapter when we discuss the energy required for the electrolysis of various compounds, and at least three should be used here. Our lamp-bank is well suited for this experiment. As the electrolyte freezes the pointer of the ammeter or galvanometer comes to zero and upon thawing again travels over the scale. Thus we get no deflection with an ordinary ammeter or galvanometer upon freezing a solvent containing ions, even when the lamp-bank is used, and we have a difference of potential of 110 volts between the terminals of the system. One might be misled in stating that we had a non-conductor just as one is accustomed to speak of glass. On going a step further, however, and substituting an exceedingly delicate galvanometer or milliammeter a good deflection through the frozen electrolyte is at once obtained. Of course it is necessary to predetermine the freezing-points of the solutions to be experimented upon and to be sure the temperature is well below that required to insure the absence of any liquid electrolyte. The slight conductivity can only be explained on account of the viscous-like behavior of ice. If ice became a *perfect solid* it would undoubtedly become a perfect non-conductor. The conductivities of crystals of copper sulphate, iron sulphate, etc., were tried and proved to be non-conductors with the most delicate instruments, unless fused, when they of course conducted as usual. A crystal is a true solid. It proves to be a true non-conductor. The passage of an electric current through chemical bodies, therefore, must be accompanied by the mechanical movement of matter. The third experiment to furnish evidence in support of ion transport is dependent upon heat convection as well as electrical convection.

HEAT CONVECTION IN ELECTROLYTIC CONDUCTION.

The apparatus illustrated in Fig. 46 was designed for the purpose of indicating the movement of ponderable material of which ions are composed, through the agency of the heat which they may be made to carry. It was reasoned that if we actually had ponderable material moving through an electrolyte, this material could be made to convey heat as well as electricity, and by the proper design of an apparatus the method could be employed for determining the absolute
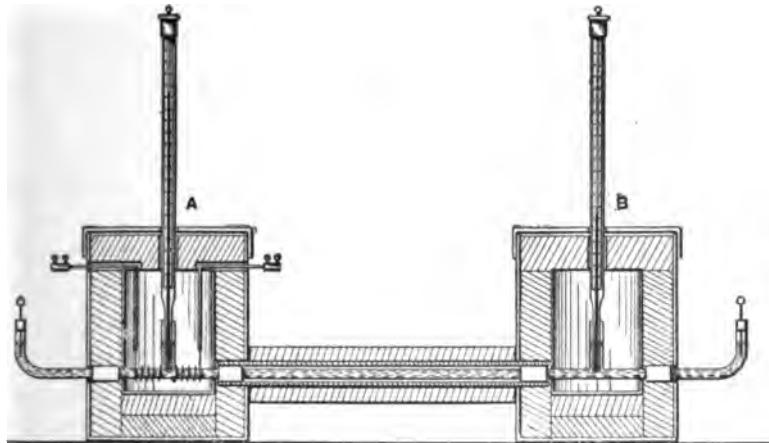
FIG. 46.—Apparatus to Show Heat Convection in Electrolytic Conduction. *A* and *B* are calorimeters made from muff boxes lined with heavy hair-felt. Beckmann thermometers dip into "T" connections in the glass tube containing the electrolyte.

velocities of ions, although in a rough way, because of sources of error difficult to overcome. At the left in the illustration is the anode calorimeter, *A*, containing a T joint receiving the bulb of a delicate thermometer. About this T joint is wound a little coil of platinum wire for the purpose of heating the contained electrolyte. This coil is attached to stout copper wires terminating in binding-sleeves outside the calorimeter, which is a pasteboard muff box lined with hair-felt. In the cathode calorimeter *B* is a similar T tube and thermometer, but without the heating-coil. The electrolyte in one experiment consisted of dilute sulphuric acid in the proportion of 20 cubic centimeters of concentrated sulphuric acid to 100 cubic centimeters of distilled water. The thermometers employed read

from 0° to 100° C. in 0.1° divisions. The platinum coil was connected to the 110-volt lighting wires through a finely graduated variable resistance, allowing of a very close control of current and heating effect. The following is an account of an experiment conducted with the electrolyte referred to.

The anode calorimeter was placed upon a higher level than the cathode calorimeter for the purpose of preventing simple convection currents due to the expansion of the water molecules within the glass T surrounded by the heating coil traveling by displacement. The experiment was started by allowing 0.1 ampere to flow through the apparatus, with a potential gradient of 1 volt per centimeter. This current was allowed to flow for three hours, when the mercury in the two thermometers appeared to reach a maximum reading. It should be stated, however, that in a special experiment conducted purely to note a special phenomenon the thermometers continued to show a rise in temperature, although at an exceedingly low rate, even after three hours, it being found that nine and one-half hours were really required before a perfect balance between the heat-energy supply and the heat-energy radiation loss through the calorimeters was reached. The rate of rise of temperature as indicated by the thermometers at the end of three hours, however, was so low as to allow of an experimental determination of the velocity of ionic travel. To determine the velocity of hydrogen ions, therefore, it is only necessary to replace the ordinary thermometer in the cathode calorimeter by an open-scale Beckmann thermometer of the most sensitive type, carefully adjusted to the temperature of the electrolyte into which it is to dip, which of course may be done from the reading on the ordinary thermometer. The apparatus is then allowed to stand for an additional hour for the new thermometer to reach a perfect equilibrium, when the current is admitted to the platinum heating-coil, the time being noted at the moment of closing the circuit. In another separate and special experiment the electrolyte in the T tube in the anode calorimeter A was kept at 90° C. for three hours without affecting the thermometer in the cathode T tube but 0.2° C., and this was due to conduction through the glass, and possibly a little convection in spite of the more elevated anode calorimeter. Water conducts itself, to a slight extent, so this error must be learned and applied as a correction. It

will be seen that this glass tube is inclosed within a second glass tube with an air-space around it, and the whole thing is in turn inclosed in a jacket of hair-felt. With the experiment under way as described it only remained to watch for the first indication of a marked rise upon the Beckmann thermometer in the cathode calorimeter. The distance between the two thermometer-bulbs was 80 centimeters. The hydrogen ions apparently arrived in one experiment twenty minutes late according to calculations as to when they were due. This tardiness may be attributed to the lack of sensitiveness of the thermometer. Undoubtedly the ions arrived on time, if the phenomenon is really due to the heat which they carry, but it remained for an accumulative action to take place before there was heat enough to affect the large mass of mercury in the thermometer. A thermopile and galvanometer would have acted quicker. So much for evidence of ion migration and mechanical movement. We are now in a position to take up electrochemical work of a more practical character and will open the next chapter with such introduction.

CHAPTER VII.

ENERGY REQUIRED IN ELECTROLYSIS. PRACTICAL FORMULA FOR COMPUTING. ELECTROLYTIC SEPARATION OF METALS. THE ROTATING ANODE IN ELECTRO-ANALYSIS.

IN the last chapter it was pointed out that whereas a given current flowing for a given time would separate chemical equivalents of electrolytes, the energy absorbed in electrolytes of different constitutions was not the same. Now, why is it that with some electrolytes more energy is required to isolate the constituent parts than with others? We have learned that 96,540 coulombs will isolate the *chemical equivalent of any electrolyte,* and we now learn that these 96,540 coulombs must be supplied at different electrical pressures for different electrolytes. The 96,540 coulombs without an electromotive force would not flow, and it is evident that we must have some electromotive force in order to have electrical energy, for the joule which is the unit of electrical energy is the product of the coulombs by the volts in an electrical circuit. We may theoretically have any amount of electrical energy we may wish by multiplying our 96,540 coulombs by volts or fractions of volts. To determine why some electrolytes require more energy (a higher electrical pressure with the 96,540 coulombs) than others, we need but to refer to the "heats of formation" of different electrolytes, and the doctrine of the "conservation and correlation of energy." By "heat of formation" of a chemical compound, we mean the number of calories liberated (and sometimes absorbed) when one gram-molecule of the substance is produced. To find the heat of formation of a chemical compound, a gram-molecule of the substance is taken and its combustion in oxygen determined. According to the principle discovered by Hess, if we know the heat of combustion of a gram-molecule of a compound, we may determine its heat of formation by subtracting the heat of combus-

tion of the compound from the heats of combustion of the constituent elements. For example, the heat of formation of methane, CH_4, is determined by measuring the heat of combustion of the compound in oxygen in a suitable calorimeter, and the heats of combustion of its elements in the same manner, and subtracting one from the other as follows:

Heat of combustion of methane, CH_4, = 211,930 calories, yielding CO_2 and $2H_2O$.

Heat of combustion of carbon, C = 96,960 calories, yielding CO_2.

Heat of combustion of hydrogen, H_4 = 136,720 calories, yielding $2H_2O$.

The heat of formation of a gram-molecule of methane is found by subtracting 211,930 calories (its heat of combustion) from 96,960 + 136,720 calories (the heats of combustion of its constituent parts) as given:

$$96,960$$
$$136,720$$
$$\overline{233,680}$$
$$211,930$$
$$\overline{21,750} \text{ calories} = \text{heat of formation of } CH_4.$$

Therefore when the gram-molecule of CH_4 is produced a definite amount of energy is liberated; and according to the doctrine of the conservation of energy, this same quantity of energy must be absorbed again before the compound can be broken up into its constituent parts. CH_4 is not an electrolyte; the compound was taken to serve as an illustration. Below we have tabulated the heats of formation of a number of chemical compounds taken from the general tables in Ostwald's "Outlines of General Chemistry." These have been converted into small calories.

There are of course many others given in a comprehensive table, including both organic and inorganic compounds, electrolytes and non-electrolytes, but it is believed that the list given includes a sufficient number of electrolytes to be of service in the laboratory. With such a table of heats of formation, and the doctrine of the conservation and correlation of energy, taken in connection with

Compounds.	Formulas.	Calories.	Compounds.	Formulas.	Calories.
Hydrochloric acid....	HCl	22,000	Ferric chloride.....	FeCl₃	96,100
Water.............	H₂O	68,400	Ferrous sulphate....	FeSO₄	235,600
Sulphuric acid.......	H₂SO₄	193,100	Nickel chloride.....	NiCl₂	74,500
Ammonia..........	NH₃	12,000	Nickel sulphate.....	NiSO₄	229,400
Nitric acid.........	HNO₃	49,100	Zinc oxide........	ZnO	85,800
Potassium hydroxide.	KOH	103,200	Zinc chloride......	ZnCl₂	97,200
Potassium chloride...	KCl	104,300	Zinc bromide.......	ZnBr₂	76,000
Potassium bromide..	KBr	95,100	Zinc iodide........	ZnI₂	49,200
Potassium iodide....	KI	80,100	Cadmium chloride..	CdCl₂	93,200
Potassium nitrate. ..	KNO₃	119,500	Cadmium bromide..	CdBr₂	75,200
Sodium hydroxide...	KOH	101,900	Cadmium iodide. ...	CdI₂	48,800
Sodium chloride.....	NaCl	97,900	Cuprous chloride. . .	CuCl₂	51,600
Sodium bromide.....	NaBr	85,800	Cuprous bromide...	CuBr₂	32,600
Sodium iodide.......	NaI	69,100	Cuprous iodide.	CuI₂	32,500
Sodium sulphate.	Na₂SO₄	328,800	Cupric sulphate.	CuSO₄	182,600
Sodium hydrogen sulphate............	NaHSO₄	267,800	Cupric nitrate......	Cu(NO₃)₂	82,300
Ammonium chloride.	NH₄Cl	75,800	Mercurous chloride.	Hg₂Cl₂	62,600
Ammonium bromide.	NH₄Br	65,400	Mercuric chloride. ..	HgCl₂	53,200
Ammonium iodide...	NH₄I	49,300	Silver nitrate.......	AgNO₃	28,700
Calcium hydroxide..	Ca(OH)₂	214,900	Lead chloride......	PbCl₂	82,800
Calcium oxide.......	CaO	131,000	Lead bromide......	PbBr₂	64,500
Calcium chloride....	CaCl₂	169,800	Lead iodide........	PbI₂	39,800
Calcium bromide....	CaBr₂	140,900	Lead sulphate......	PbSO₄	216,200
Calcium iodide......	CaI₂	107,300	Lead nitrate.......	Pb(NO₃)₂	105,500
Magnesium chloride .	MgCl₂	217,300	Stannous chloride...	SnCl₂	80,800
Magnesium oxide....	MgO	143,900	Stannic chloride. ...	SnCl₄	127,300
Magnesium hydroxide	Mg(OH)₂	217,300	Auric chloride......	AuCl₃	22,800
Aluminium hydroxide	Al(OH)₃	297,000	Aurous chloride....	AuCl	5,800
Aluminium chloride..	AlCl₃	151,000	Aurous bromide. ...	AuBr	− 100
Aluminium bromide..	AlBr₃	119,700	Aurous iodide......	AuI	− 5,500
Aluminium iodide ...	AlI₃	70,400	Chloroplatinic acid..	H₂PtCl₆	163,200
Ferrous chloride.....	FeCl₂	82,100	Bromoplatinic acid..	H₂PtBr₆	88,400

our important constant of 96,540 coulombs, we should be able to calculate the minimum voltage or electromotive force necessary, and consequently the energy required, to break up any chemical compound by electrolysis. It is simply converting heat energy into electrical energy. We must of course know the relation between the calorie and the joule, and should commit this to memory as a very important figure:

$$1 \text{ joule} = 0.00024 \text{ Calorie}$$
$$1 \text{ joule} = 0.24000 \text{ calorie}$$

Let us take one or two examples and work them out, developing a practical working formula for future use. We have already learned that electrolytes may be either chemical compounds in solution or in a state of igneous fusion. As we have dealt with many electrolytes dissolved in water, let us consider an electrolyte

in a state of fusion by heat. Let us first take an electrolyte con-
sisting of monovalent constituents, and consider it theoretically.
Common salt, or sodium chloride, will serve our purpose, with its
monovalent sodium linked to the monovalent chlorine. In cal-
culating the minimum voltage necessary to isolate a chemical equiva-
lent of sodium and chlorine, and the energy necessary to effect the
electrolysis, we must consider the gram-molecule as the basis of
our calculation, which in the case of sodium chloride is 58.5, since
sodium has an atomic weight of 23, and chlorine 35.5. There-
fore 23 + 35.5 = 58.5. 58.5 grams of sodium chloride is the
gram-molecule of the salt. Glancing at the table of "heats of
formation" for the value found for sodium chloride, we see it to be
97,900 calories. When 23 grams of sodium combine with 35.5
grams of chlorine, therefore, to form 58.5 grams of sodium chloride,
97,900 units of heat are set free. According to the doctrine of the
conservation of energy, in order to decompose these 58.5 grams
of sodium chloride, an amount of energy equal to that liberated
at the time of formation must be expended upon it to break it
up. How much electrical energy, for instance, is the equivalent
of 97,900 heat units? The heat unit is the calorie, and we have just
learned that 0.24 Calorie is equal to the joule. 97,900 calories
divided by 0.24 therefore gives us the joules necessary to effect the
electrolysis.

$$\frac{97,900}{0.24} = 407,916 \text{ joules.}$$

We have learned that the passage of 96,540 coulombs will set
free the chemical equivalent of any electrolyte, and we see from the
above exposition that 407,916 units of electrical energy are neces-
sary. In order that the passage of 96,540 coulombs should repre-
sent the expenditure of 407,916 joules, they must be supplied at an
electrical voltage or potential of

$$\frac{407,916}{96,540} = 4.22 \text{ volts.}$$

To liberate 23 grams of sodium and 35.5 grams of chlorine,
therefore, from 58.5 grams of sodium chloride, we will have to
expend 407,916 joules of electrical energy, and it will be necessary

to have a voltage of at least 4.22 volts before an electrical current
can be made to pass through.   Let us take the case of a compound
with a divalent constituent, for example magnesium chloride ($MgCl_2$),
from which to theoretically and practically, if we may so speak, sep-
arate the chlorine from the metal.   By referring again to our table
of formation heats, we find for the gram-molecule of magnesium
chloride that 217,300 calories are liberated.   We have therefore:

$$\frac{217,300}{0.2400} = 905,415 \text{ joules.}$$

Now we are dealing with a divalent electrolyte, and according
to Faraday's law it will require the passage of 96,540 + 96,540 cou-
lombs to separate the constituents.   This gives us:

$$\begin{array}{r} 96,540 \\ 96,540 \\ \hline 193,080 \text{ coulombs,} \end{array}$$

which must be divided into 905,415 joules in order to obtain the
minimum voltage

$$\frac{905,415}{193,080} = 4.68 \text{ volts.}$$

It is evident that these minimum voltages are dependent upon
the degree of accuracy attained in the determination of the heat of
formation of the compound in the calorimeter, which, of course,
is purely a thermochemical operation.   It must be stated, however,
as a matter of fact in an actual experiment with a fused electrolyte,
that the calculated voltages are a little high, which is accounted
for by the high temperatures of the fused compound.   At the tem-
peratures of igneous fusion the heats of formation have a lower
value, apart from the fact that compounds are dissociated in the
fused state.   When in a state of igneous fusion, therefore, a voltage
of something less than the calculated pressure will drive the elec-
trical current through.   Let us perform the experiment of electri-
cally separating the metal magnesium from the chloride, and measure
the electrical energy required.   Fig. 47 shows the equipment which
we can use to good advantage, both as a laboratory method of pro-
ducing the metal, and also as a brilliant lecture experiment, where
a large mass of the metal is produced and hammered out and ignited

to produce the dazzling magnesium light. At the left in this illustration we have the motor-generator, with the controlling rheostats
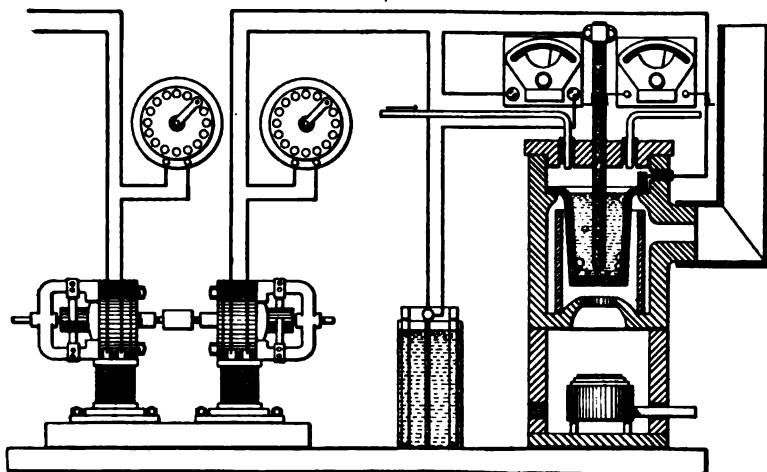
FIG. 47.—Experimental Equipment for Lecture-room or Laboratory for Electrically Isolating Metallic Magnesium from its Chloride. Motor-generator with rheostats at left. Copper voltameter in center, and small fusion-furnace at right.

for supplying a heavy current at low electrical pressure. The furnace is of the small gas-fusion type, which contains an iron pot for the electrolyte, and which, as can be seen, is made the cathode. The anode consists of a large rod of carbon passing through a tight-fitting cover. A large copper voltameter is depicted in the center for determining the number of coulombs passed, and electrical instruments are connected to the leads to indicate the voltage and current strength. For our experimental purposes an artificial carnalite will best serve our purpose for the electrolyte. The composition of this mineral may be set down as follows:

$$KMgCl_3, 6H_2O = KCl + MgCl_2 + 6H_2O = MgCl_2 \ 34.2,$$
$$KCl \ 26.9, \ H_2O \ 38.9 = 100.$$
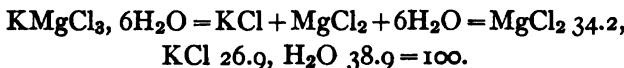
For our purpose we can prepare an easily-fused artificial carnalite by evaporating to dryness on a water-bath a solution of

> 400 grams of crystallized magnesium chloride,
> 150 grams of potassium chloride,
> 60 grams of ammonium chloride.

This residue may be placed in a large salt-mouthed bottle for use as required. For an experimental run the iron vessel in which the electrolysis is to be carried on is carefully cleaned on the inside by means of sandpaper, to remove any rust and to produce a bright metallic surface from which the magnesium is easily separated. This iron pot is so connected as to form the cathode, and is placed in the furnace and the gas lighted. A small piece of charcoal is put in the pot to prevent oxidation as it heats up. When a faint red glow is seen in the bottom of the iron pot, the artificial carnalite is slowly added, allowing each addition to fuse and run before the next portion is added. The pot may in this way be nearly filled, when the carbon anode is placed in position through the top. Now, as magnesium is a very light metal and often rises to the top of the electrolyte after being isolated, when it takes fire and is destroyed, it is necessary to protect it. For this purpose a tight-fitting top is the best precaution, fitted with asbestos plugs through which hard-glass tubes pass as indicated in the drawing. By means of these tubes a gas can be passed which displaces the oxygen present, and prevents the combustion of the magnesium. The present writer has connected these glass intake-tubes direct to the city lighting gas-supply with much success, allowing the coal-gas and chlorine to be led away to a hood. In this way we have the magnesium completely protected from possibilities of combustion, since coal-gas being a mixture of hydrocarbons, etc., does not support combustion. For an experiment, therefore, the top is placed in position after the chlorides have fused to a clear, transparent liquid, and coal-gas is passed through the space over the electrolyte when the electrical current is started. The magnesium separates smoothly, and may be ladled out and cast into molds, care being taken to allow the electrolyte to cool down considerably before exposing it to the air, as it is very likely at high temperature to take fire and burn with its characteristic dazzling light. Of course, for a full efficiency determination of such a process an accurate gas-meter, with the necessary observations for gas temperature and atmospheric pressure, should go in with the burner. For a complete physical and electrical study of the isolation of magnesium, the heat value of the fuel-gas per cubic foot should be determined by means of a suitable calorimeter. There are several calorimeters

especially designed for determining the heating value of gaseous fuels. With our copper voltameter and reliable voltmeter we will be in possession of the essential data for interesting figures taken in connection with the weight of metal produced. This experiment is capable of going still further, using the liberated chlorine, for example, to prepare chloride of lime. For this purpose we should prepare a lead box with lead shelves, upon which we can lay out a quantity of moist slaked lime. The temperature is not allowed to rise above 25°, which is controlled by diluting the chlorine passing into the chamber with air. The constitution of chloride of lime is not known with certainty, but the action between the chlorine and the moist slaked lime may be represented as follows:

$$Ca(OH)_2 + Cl_2 = CaCl(OCl) + H_2O.$$
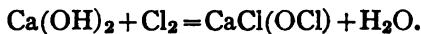
Thus a very pretty by-product may be obtained at the time of isolating the metallic magnesium.

Let us take a case of a non-igneous electrolyte, and calculate the minimum voltage required. We are almost unlimited in a selection of these cases, and for this reason a novel case of electrolysis as conducted by the author, to show that sulphuric acid consists of hydrogen, oxygen, and sulphur, may be of special interest. This is an interesting lecture experiment for both beginners in general chemistry and for those advanced in physical chemistry as well. We all know that dilute sulphuric acid electrolyzes into hydrogen and oxygen gases, and that these gases are liberated in the proportion of two volumes of hydrogen to one volume of oxygen. The writer has conducted numerous experiments with concentrated sulphuric acid, and by the proper adjustment of concentration, current density, temperature, etc., has been able to electrolyze the acid into hydrogen, oxygen, ozone, and free sulphur, and at elevated temperatures into hydrogen, oxygen, sulphur trioxide, and ozone. Fig. 48 illustrates the apparatus for conducting such electrolysis. At the left we have a bell jar covering the beaker containing the strongest chemically-pure sulphuric acid over a dehydrating agent, such as calcium chloride. A thermometer is fitted through the stopper as shown, and the electrical equipment includes · electrical instruments for observing the energy conditions. The

motor-generator is shown at the extreme right with the controlling
rheostats, although the lamp-bank serves equally well, if not better,
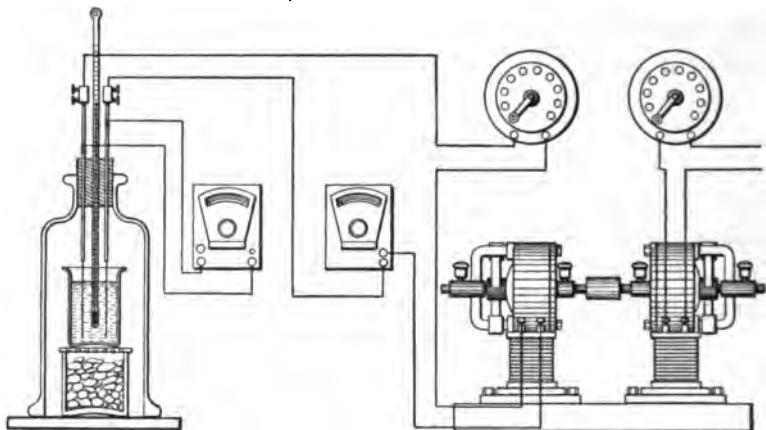
FIG. 48.—Apparatus for the Electrolysis of Concentrated Sulphuric Acid to obtain as
Electrode Products Hydrogen, Oxygen, Ozone, and Free Sulphur which may be
Exhibited upon the Anode and be Burned. Therefore, sulphuric acid may be
directly broken down into its elements.

for this particular experiment. Upon passing a sufficiently heavy
current through the concentrated acid we get free sulphur, together
with ozone, oxygen, and hydrogen, as indicated in the accom-
panying equation:

$$H_2SO_4 = H_2 + O + O_3 + S.$$
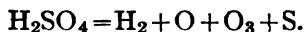
The sulphur deposits upon the anode and may be burned with its
characteristic blue flame before a class to show its presence. The
ozone may be detected by moistening a piece of filter-paper in starch
and potassium iodide preparation, and holding it near the anode
during electrolysis. The hydrogen may be collected and burned.
The minimum voltage for conducting such an experiment may
be calculated by means of our formula to a fair degree of precision.
As we are now in a position to follow theoretically as well as practi-
cally an electrochemical process, the writer introduces what he
believes to be the "mechanism" of this particular electrolysis. In
all our practical work we must endeavor to account theoretically
for the phenomena involved in practice, for it is the man with the
insight into both theory and practice who makes the best invest-

tigator. Having calculated the minimum voltage and energy required, and conducted an actual electrolysis, we should certainly endeavor to express that which takes place in concise and scientific manner. In the almost classic case of sulphuric acid and water, the acid is believed to dissociate into the ions

$$\overset{++}{H_2} \text{ and } \overset{--}{SO_4}.$$

The $\overset{--}{SO_4}$, instead of being set free, decomposes the water present, as indicated as follows, taking up the two atoms of hydrogen present, to form sulphuric acid and liberating oxygen. As the result of certain research work upon the concentrated acid, it is believed to dissociate into the ions $\overset{+}{H}$ and $\overset{--}{HSO_4}$.
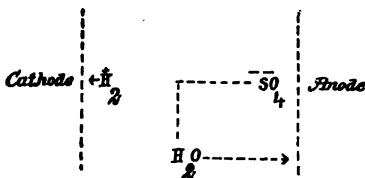
Now, according to recent research upon the conductivity of pure water, water itself is found to be slightly dissociated (about one molecule in a million being broken down thus: $\overset{-}{H}\overset{+}{OH}$) and taking this fact into account, we may have upon this basis the liberation of two volumes of hydrogen and one volume of oxygen equally well accounted for in diagram.
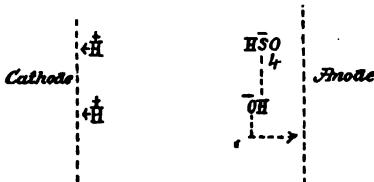
Now let us write the structural formula of sulphuric acid, and endeavor to represent the "mechanism" of electrolysis when we obtain hydrogen, oxygen, ozone, and free sulphur.

$$\begin{array}{l} H-O-\\ H-O- \end{array}S\begin{array}{l}=O\\ =O. \end{array}$$
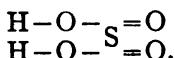
Here we have the sulphur acting with the valence of six, and a
scheme indicating the linking of the acid.   How can it electrolyze
and give such products?   The following diagram shows the prob-
able manner taking dissociated water into account:
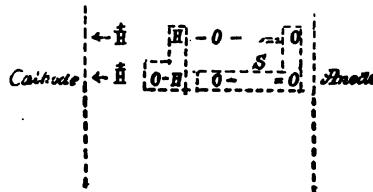
Here we also have the formation of a molecule of water within the
electrolyte.   If, however, the temperature is allowed to rise above
105° C. we obtain hydrogen, oxygen, and sulphur trioxide, with
the formation of a molecule of water within the electrolyte as follows:
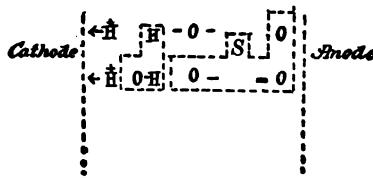
So much for this side of electrolysis and the part played by
minimum voltage, or electrode tension as a factor in experimental
as well as in commercial work.

ELECTROLYTIC SEPARATION OF METALS.

Under the present heading we will take up the art of electro-
analysis, and separate one metal from another, when both exist
in the same solution, through the proper adjustment of electrode
tension.   Fig. 49 shows a plan for accomplishing this.   Here we
have a platinum dish resting upon a platinum plate, connected with
the negative wire of a storage-battery and variable rheostat.   A
disk of platinum welded to a platinum wire is suspended in the
dish to serve as anode, and is connected in turn with the battery.
A delicate ammeter and voltmeter complete the equipment, and
are joined up as shown.   Only instruments of delicacy and pre-
cision are applicable for this class of work, and a rheostat capable

of fine graduations is absolutely essential.   The cells of the battery
must be so arranged that one or more may be joined in series in a
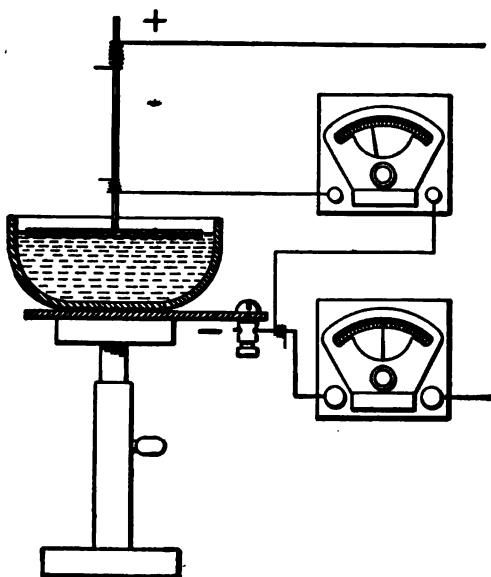
FIG. 49.—Method of Separating Metals by Electrodeposition through Adjustment
of Electrode Tension.

convenient manner.   Having set up the apparatus, we are in a
position to undertake some experimental work.   Fig. 50 illustrates
a practical working equipment for separating one metal from an-
other on the basis of electrode tension.   A platinum dish and plati-
num strip acting as the cathode and anode respectively are shown
in the center.   Readers of electrochemical literature will in this
connection come across the terms "polarization" and "polariza-
tion current," etc., which refer to the back electromotive force
or tension necessary in order to force a current through an electro-
lyte.   Therefore, polarization may be under tood to refer to the
minimum voltage necessary to effect an electrolysis.   Le Blanc
made many c reful researches upon the electrode tensions neces-
sary to decompose various salts, acids, and bases when in solution,
and it may be easily seen that we may separate one constituent
from another in an electrolyte by carefully adjusting the electrode
tension to fall between the two different values for the different

electrolytes. Le Blanc found the following values for normal solutions:

	Volts.		Volts.
$ZnSO_4$	2.35	$Cd(NO_3)_2$	1.98
$ZnBr_2$	1.80	$CdSO_4$	2.03
$NiSO_4$	2.09	$CdCl_2$	1.88
$NiCl_2$	1.85	$CoSO_4$	1.92
$Pb(NO_3)_2$	1.52	$CoCl_2$	1.78
$AgNO_3$	0.70	H_2SO_4	1.67
HNO_3	1.69	HCl	1.31
$NaOH$	1.69	KOH	1.67
NH_4OH	1.74	HBr	0.94

This is of course only a partial list, but will be sufficient to serve as a useful guide in the laboratory. Any attempt to outline methods
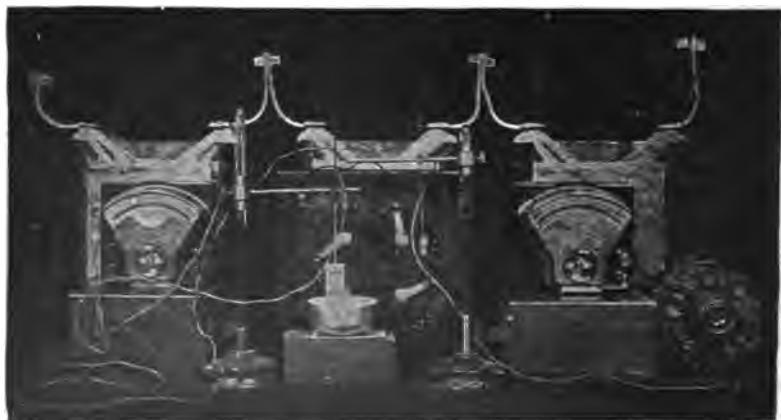
FIG. 50.—The Separation of Metals by Adjustment of Electrode Tension. Rheostats, storage-batteries, and electrical instruments are shown here in practical operation in the laboratory.

of electro-analysis would be incomplete at this time without introducing the attractive and useful device known as the rotating anode. Suppose, for example, it is wished to determine copper in the electrolytic way, that is by deposition upon a platinum dish. According to the old scheme, we had the dish and a stationary anode. With this arrangement it was necessary to work with a feeble current, or else the deposit of copper would come down dark and non-adherent. For this reason it took many hours, very often, to produce complete precipitation. With the rotating anode, the current strength can be enormoulsy increased, and yet obtain a beautiful pink adherent deposit of copper in a correspondingly shorter time. Here

we have an electric motor properly wound to run on a storage-battery circuit, *or else especially wound to run on the electric-lighting circuit with lamps in parallel. Do not try to use a very small motor.* Procure one several sizes larger than is really necessary to revolve the anode, for it can be much more easily controlled through the agency of our lamp-bank, or a special short bank as illustrated at the extreme right in Fig. 51. Here the addition of one lamp will give the motor
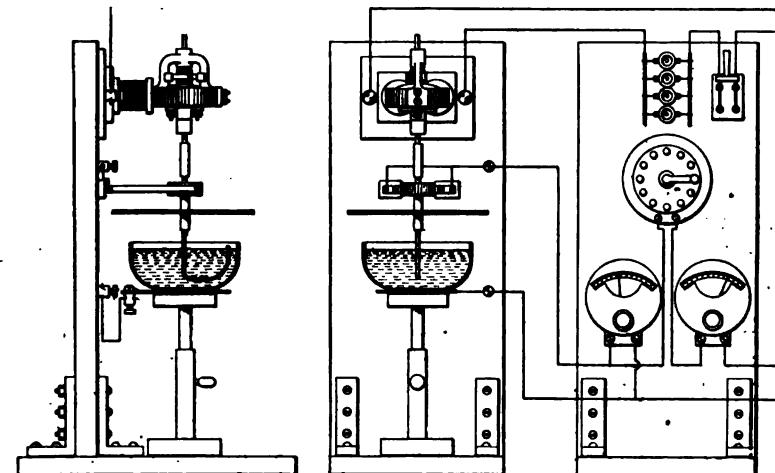
FIG. 51.—Easily-constructed Rotating Anode for Rapidly Conducting Electro-analysis. With this equipment an electro-analysis may be completed in a few minutes, which would require several hours to accomplish in the old way.

a certain speed, which may be increased by the addition of others. From thirty to one hundred and twenty revolutions per minute have been found to be excellent speeds, although higher speeds may be used with advantage so long as there is no danger of losing electrolyte by its spinning out of the dish. A large disk just above the platinum dish should be included in the equipment, to prevent anything falling into the dish from the commutator and contact brushes above. The rest of the make-up is so simple that the illustration should serve to make it clear. A few words concerning the principle upon which the rotating anode accomplishes its rapid precipitation may be given here. The main thing accomplished by the rotating anode is to keep the solution homogeneous in character.

Let us take the case of a solution of copper sulphate. If a comparatively feeble current of electricity be passed through an electro-

lyte consisting of copper sulphate for a long time, there are concentration changes set up.   If we use copper electrodes the anode loses in weight just as much as the cathode gains, and there is at all times in the solution the same amount of copper, or to put it in other words, there is always the same number of copper ions in solution. Now, even with the use of copper electrodes and a constant number of copper ions present in the solution, concentration changes will be set up if the current is allowed to flow for any considerable length of time.   In such an experiment it is found with copper sulphate, for example, that we get an increase of concentration at the anode and a decrease of concentration at the cathode.   Fig. 52 represents the condition of affairs in a vertical glass tube containing copper electrodes and an electrolyte of copper sulphate.   The shaded portion represents the concentration of the solution about the anode. Now, if this took place, as it does with a platinum dish and stationary anode, the copper ions become so few, or in other words the electrolyte becomes so poor in copper about the cathode dish, that we are held down to the use of a feeble current or there will be trouble in getting the adherent, pink deposit, so necessary for all accurate determinations of copper by electro-deposition.   How can these concentration changes be overcome?   The rotating anode accomplishes this perfectly, and enables us to keep a constant supply of copper ions about the cathode dish, and allows consequently of a heavy current being employed.   How can we explain the concentration changes?   Fig. 53 shows by diagram how such accumulation of copper ions about the anode is accounted for according to Hittorf.   The changes in concentration calculated from one of Hittorf's researches are shown in this diagram.   Here the white circles represent the anions and the black circles the cathions, and the dotted horizontal line indicates merely the middle of the solution in the vertical containing vessel.   The electrolyte is perfectly homogeneous before the electric current is passed, as is seen by an equal number of anions and cathions respectively on each side of the line.   In the figure we have nine upon each side.   Now allow the current to pass for a given time.   We know that different ions have different velocities, and consequently the Cu ions will move in one direction at a different rate from the SO_4 ions moving in the other direction.   It is very often confusing to the student

to understand how we can have such concentration changes due to different velocities of the ions when we have the same equivalents of ions liberated at anode and cathode respectively. No cathion can separate at the cathode until an anion separates at the anode, and for each and every ion which is liberated at one electrode there must be a corresponding ion liberated at the other. There may,
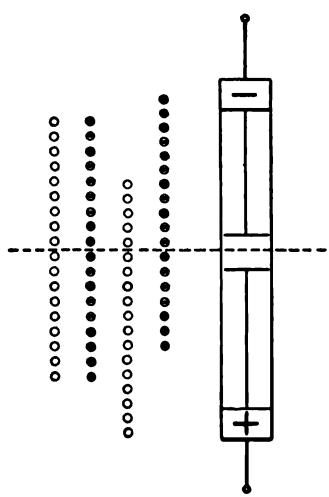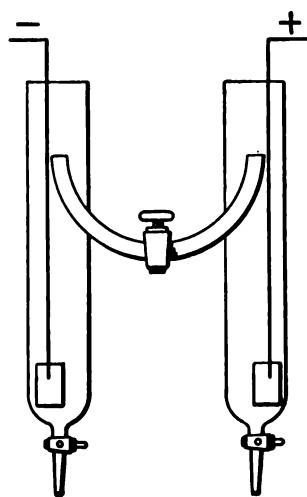
FIG. 52.   FIG. 53.   FIG. 54.

FIG. 52.—Experiment with Copper-sulphate Solution to show Concentration Changes wrought by a Feeble Current Flowing for a Long Time. The electrodes are of copper.

FIG. 53.—Diagram Representing Hittorf's "Transport Numbers." From Hittorf's researches the relative velocities of ions are determined experimentally, by concentration changes.

FIG. 54.—Approved Apparatus of Mather and Jones for Experimentally determining the Relative Velocities of Ions Based upon Concentration Changes.

of course, be the case where we have one divalent ion separating at one pole and consequently two univalent ions separating at the other. Faraday's law teaches us this. As a result of the different velocities, while we have an anion liberated for every cathion, we may have a banking up of the swifter kind of ions, and so to speak, ready to discharge. This is illustrated in the little diagram at the right, where we have thirteen anions across the dotted line and

only eleven cathions across the dividing line in the opposite direction. Such concentrations may be practically shown by experiment with a piece of apparatus as illustrated in Fig. 54, as devised by Mather, working with Jones. Here a copper-sulphate solution, for example, may be electrolyzed, and the solution drawn off from the two tubes respectively and analyzed for concentration. Knowing the original concentration of the homogeneous electrolyte, the number of coulombs passed, and the respective concentrations of the respective anode and cathode tubes, we have all the data for determining the relative velocities of the two ions. This is a very practical piece of apparatus, and with it very interesting concentration changes may be studied.

CHAPTER VIII.

IMPORTANT CONDITIONS TO BE NOTED IN ELECTROCHEM-
ICAL OPERATIONS. CAUSTIC SODA AND CHLORINE FROM
SALT. ELECTROLYTIC PRODUCTION OF WHITE LEAD.
ELECTROLYTIC PRODUCTION OF CADMIUM YELLOW.
ELECTROLYTIC PRODUCTION OF MERCURY VERMILION.
ELECTROLYTIC PRODUCTION OF SCHEELE'S GREEN.
ELECTROLYTIC PRODUCTION OF BERLIN BLUE.

VARIOUS controlling conditions must be observed in all electro-
chemical operations, and be recorded in connection with every piece
of experimental work. There are many governing adjustments or
conditions in electrolysis, without a working knowledge of which the
student will be unable to meet with any notable success in carrying
out a determination, or be able to obtain the same result twice in
any undertaking. One of the most important factors in all electro-
chemical work is that of "current density," and because of its great
moment and importance it will be dealt with at the opening of this
chapter. Current density depends upon the ratio of electrode area
to the current flow in an electrolytic cell. We may have high-current
density at both electrodes, or low-current density at both electrodes,
or else high-current density at one of them and low-current density
at the other. Fig. 55 has been designed to make this clear. At the
left in this diagram the anode is simply a thin platinum wire affording
but small surface from which the electric current can leave to enter
the electrolyte, whereas the cathode is a platinum sheet affording
a large surface for the same current to be conducted from. At the
right in the same diagram the conditions of current density are
just reversed. Now the point of interest lies in the fact that adjust-
ments of current density have an important effect upon almost all
electrochemical operations, determining the character of the electrode
products, as well as the chemical change which may take place

throughout the entire electrolyte. Oxidation and reduction are two of the most important chemical phenomena, and yet the oxidation or reduction of an electrolyte may be brought about by the same electric current, the only difference in its application being that of current density. The following rule should be learned by all electrochemical students:

Oxidation is effected by using concentrated electrolytes and by a low-current density at the anode, as depicted in the right-hand cell in the illustration. Reduction is effected by using concentrated
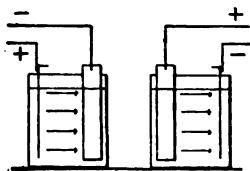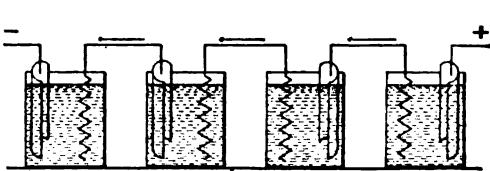
FIG. 55.　　　　　　　　　　　　　FIG. 56.

FIG. 55.—Diagram to Show Two Different Conditions of Current Density. At the left there exists high-current density at the anode and low-current density at the cathode. In the cell depicted at the right we have low-current density at the anode and high-current density at the cathode.

FIG. 56.—Four Cells in Series receiving a Common Current, but because of Dissimilar Current Density Adjustments, Electrolytes in the Several Cells will Yield Different Decomposition Products. The electrolysis in the two cells at the left will be the same, but will differ from the products in the two cells at the right.

electrolytes and a low-current density at the cathode, as depicted in the left-hand cell in the illustration.

It will, therefore, be fully appreciated how very important it is to note and take fully into account the conditions of current density in any piece of experimental work. Fig. 56 illustrates four cells in series, the whole system, therefore, receiving a common electric current. The conditions of current density, however, are not the same, and we will obtain different results in the two cells at the right from those in the two cells at the left. To test this we can perform the following simple experiment, using a solution of oxalic acid for the electrolytes, to which has been added a quantity of sulphuric acid. Take 60 grams of oxalic acid to the liter of water, and add 50 grams of sulphuric acid, and place an equal portion of this solution in each of the four cells. A current of about half an ampere is allowed to flow for an hour, when the oxalic solution in each cell is determined by means of permanganate of potassium. Oxidation

will be found to have taken place in the two right-hand cells if the current adjustment is as shown in the diagram, and is equal for each cell. At the left there will be no notable increase, although we do not get a correspondingly great reduction. It should be stated that these current density conditions exert a strong tendency to oxidize and reduce respectively, but of course all electrolytes are not oxidizable or reducible any more than many compounds are which go to make them up. We know that oxidation is usually accompanied by liberation of heat, and it is therefore of great moment to know both the anode and cathode temperatures in an electro-chemical research. Fig. 57 illustrates the plan of the author for
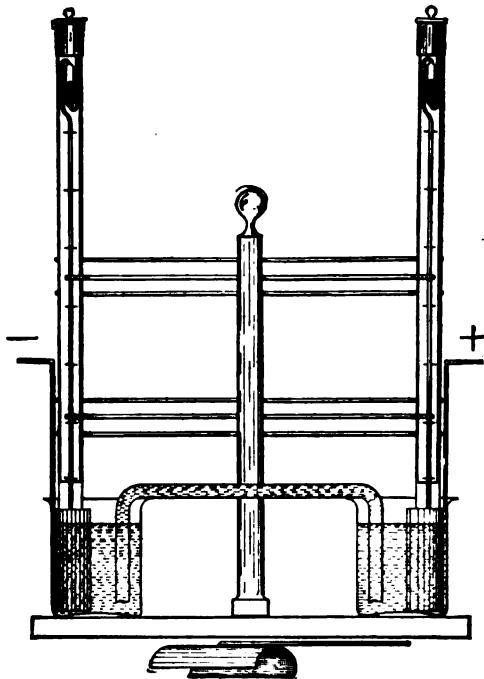
FIG. 57.—Author's Arrangement of Two Sensitive Beckmann Thermometers to Study Anode and Cathode Temperatures, when Making a Research upon an Electrolyte.

investigating such differential heat liberation. What are some of the other important conditions to be observed? They are many and vital, and it is deemed that a concise tabulation of them, as arranged by the author for use in the laboratory, will be perhaps a

good way of presenting them. In making any kind of a research upon a solution when subjected to the action of an electric current, the conditions tabulated here should be taken account of. If a piece of experimental work is to be undertaken, a neatly-kept notebook should of course be opened, and a careful record kept of each thing observed, together with all the existing conditions. It will be necessary to make a number of repeated special runs to secure all the data as advised in the accompanying table, as there are too many conditions to be usefully observed and recorded during any one run. For example, a special run may have to be made for differential temperatures, another for specific gravity determinations, etc. In several runs the following table may be compiled for reference. This particular table was the result of the author's work upon sulphuric acid.

Duration of run.....................	One hour
Compound electrolyzed..............	H_2SO_4
Character of solution................	No solution
Sp. gr. before electrolysis............	1.84664
Sp. gr. after electrolysis.	1.84001
Quantity of compound taken..........	100 c.c.
Character of apparatus.	See illustration
Dimensions of cell...................	7×8 cm.
Source of electricity.................	Motor-generator
Temperature of electrolyte............	21.5° C.
Temperature at anode................	21.5° C.
Temperature at cathode..............	21.5° C.
Amperes flowing.................. ...	4.250
Volts indicated......................	16.00
Area of anode immersed..............	4 sq. cm.
Area of cathode immersed............	4 sq. cm.
Current density at anode.	$A_{100} = 106.2$
Current density at cathode............	$C_{100} = 106.2$
Distance between....................	3 cm.
Phenomenon at anode...............	SO_2 and O
Phenomenon at cathode..............	Hydrogen
Phenomenon between................	Floating S in 3 mins.
Secondary action at anode.	None at once
Secondary action at cathode..........	None at once
Secondary action between............	None
Later phenomenon at anode..........	SO_3 at 103.5° C.
Later phenomenon at cathode.........	None
Later phenomenon between...........	Increased S
Material of anode.	Platinum
Material of cathode..................	Platinum
Material of containing cell............	Glass
Special peculiarities..................	

Many operations, of course, will not require the setting down of so many data, but for all research purposes the student will do well to tabulate his facts as completely as possible. We are now in a position to produce electrolytic preparations, and a few interesting examples for laboratory practice are given here.

CAUSTIC SODA AND CHLORINE FROM COMMON SALT.

This is one of the first laboratory exercises the student in experimental electrochemistry should take up in the way of preparations. The experiment is a very practical and easily carried out introduction to electrochemical manufacture. The apparatus as illustrated in the photograph in Fig. 58 is easily and quickly put together in any laboratory, and serves a most useful purpose in many cases of electrolysis where the anode gas is to be collected. The apparatus simply consists of a large beaker glass containing a good-sized porous pot, about which a cylinder of nickel-wire gauze is placed to form the cathode of the cell. A cylindrical lamp-chimney is next procured, and fitted with a heavy rubber stopper, through which passes a rod of carbon to serve as the anode. There is a second hole in this stopper, to receive a small glass tube, through which the chlorine escapes from the glass lamp-chimney chamber. The rubber stopper should be given several coats of paraffin wax inside and out with a good brush dipped into a melted mass. The electrolyte consists simply of a saturated solution of common salt in water, and our lamp-bank with two or three lamps in parallel in connection with an electric-lighting system completes the equipment. Chlorine gas escapes copiously from the anode chamber, and a corresponding quantity of sodium hydroxide is formed in the cathode chamber. Hydrogen of course escapes from the nickel-wire gauze when the salt breaks up in accordance with the following equation:

$$2NaCl + 2H_2O = 2NaOH + H_2 + Cl_2.$$

The chlorine should be led into a lead-lined box containing lead shelves holding moist calcium oxide, as outlined in the electrolysis of magnesium chloride, for the simultaneous production of chloride of lime, or the chlorine may be led into water to saturate it for

bleaching purposes. The liquid from the cathode chamber is poured off after the run, and evaporated to dryness in a porcelain

FIG. 58.—Large Beaker Arranged with Porous Pot and Glass Anode Chamber for Producing Caustic Soda and Chlorine from Common Salt.

dish to obtain the solid caustic soda. This experiment can and should be run quantitatively by including a copper voltameter in series with it, and noting the fall in voltage between the electrodes, in order that we may state the number of joules absorbed per gram of sodium hydroxide produced, and per gram of bleaching-powder, etc. The porous-pot partition in this apparatus plays a most important part, as it keeps the chlorine set free from acting upon the caustic soda formed to produce another compound, namely, sodium hypochlorite. As the use of porous pots is of great importance in a great many electrolytic operations as well as in research and investigations, a group of the various desirable shapes and sizes has been photographed, which constitutes Fig. 59. A good supply of these should be at hand in every electrochemical laboratory.

ELECTROLYTIC PRODUCTION OF WHITE LEAD FROM METALLIC LEAD ELECTRODES.

A very beautiful electrolytic preparation is that of white lead from the metallic lead electrodes in an electrolytic cell. White lead, or technically the basic lead carbonate, has the following formula, which is sometimes called hydrate-carbonate of lead:

$$2PbCO_3.Pb(OH)_2.$$

For our purpose we will require either a rectangular glass jar or cell, or else a large beaker glass, and heavy sheet-lead electrodes. The adjustment for current density in this preparation is the same for both electrodes, that is, they are of the same immersed area in the electrolyte. A good working current density for this experiment

is 0.5 ampere for every 100 square centimeters of anode and cathode surface immersed. The expression for current density is frequently met with in abbreviated ways, which the reader of electro-

FIG. 59.—Porous Pots of Various Shapes and Sizes which should be Supplied to every Electrochemical Laboratory.

chemical processes will come across, and they are therefore given here in their usual manner, in order that he may become familiar with them. For example, the following expression,

$$Da = Dc = 0.5 \text{ ampere per 100 square centimeters,}$$

means that the anode current density is the same as the cathode current density, and that they each equal 0.5 ampere per 100 square centimeters of immersed surface, measuring usually both sides of the two electrodes in making the calculation of area. The expression

$$N.D._{100} = 0.5 \text{ ampere}$$

will also be met with, expressing the current flow from an electrode for every 100 square centimeters of electrode area.

Let us now prepare a few grams of electrolytic white lead, and tabulate the data in such concise form that we should at any time be able to repeat the experiment with certainty, or be able to direct others to do so. The electrolyte in this case will be 12 grams of sodium chlorate and 3 grams of sodium carbonate dissolved in 1 liter of water. A rectangular glass cell, two sheet-lead electrodes, and our lamp-bank equipment in connection with a lighting circuit will meet the electrical requirements, and it only remains to fit up a generator for the production of carbon-dioxide gas from dilute

acid and fragments of marble. The electrolysis is conducted at
about 20° C., and a slow current of carbon-dioxide gas is led into
the electrolyte in contact with the cathode, the electrolyte being
kept in motion by a stirrer. The white lead flows down in thick
clouds from the anode to the bottom of the cell, and may be col-
lected in a little bag of tow attached to the electrode, when it may
be removed and ground with oil to make the well-known basis for
oil colors. The yield of white lead in this experiment is excellent,
and the operation forms a very pleasing lecture preparation, for
the formation and falling down of the white lead from the solution
is very beautiful and pleasing, especially when one is familiar with
the unattractive old Dutch method, dependent upon the chemical
action of the vapors of acetic acid, carbonic acid, and oxygen upon
masses of lead in pots, which must be buried for long periods of
time in horse-manure, in order that fermentation may assist chemi-
cal action by an increase in temperature. Our electrolytic process
may be made continuous, and has attained commercial importance
in recent years. In this experiment the electrolyte contains two
salts in very dilute solution. The sodium chlorate, which is present

in four-fifths of the total amount, has as an anion $\overline{ClO_3}$ which forms
a soluble salt with the anode lead, producing lead chlorate, which

passes into solution. The sodium carbonate, whose anion $\overline{CO_3}$
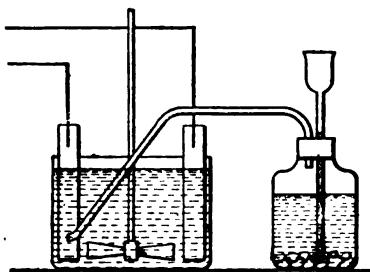
FIG. 60.   FIG. 61.

FIG. 60.—Experimental Apparatus for the Electrolytic Production of White Lead
    from Lead Electrodes.
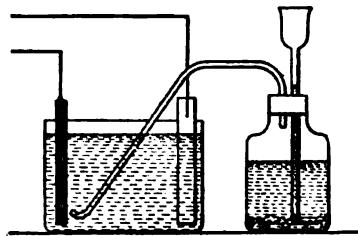
FIG. 61.—Experimental Apparatus for the Electrolytic Preparation of Cadmium Yel-
    low from a Stick Cadmium Anode.

forms an insoluble salt, lead carbonate, produces the precipitation.
As a result of using such proportions, the insoluble salt does not

deposit at once upon the anode, but is precipitated some distance from it, and does not give trouble by forming an insoluble crust on the electrode. The caustic soda produced at the cathode combines with the carbon-dioxide gas which is bubbling through the solution, and regenerates sodium carbonate. Fig. 60 will make the apparatus clear. Here in the center of the cell is shown a stirrer to be operated by a small electric motor when it is desired to show the experiment in the lecture-room. Below will be found tabulated the principal data in such an experimental run:

Duration of run.	1 hour
Electrolyte.	12 grams $NaClO_3$,
	3 grams Na_2CO_3
	in 1 liter water
Character of apparatus.	See figure
Dimensions of cell.	8 cm.$\times$20 cm.$\times$20 cm.
Source of electricity.	Lighting circuit and
	lamp-bank
Temperature of electrolyte.	20° C.
Amperes flowing.	0.5 ampere
Volts indicated.	60
Area of anode immersed.	100 sq. cm.
Area of cathode immersed.	100 sq. cm.
Current density at anode.	$N.D._{100}$=0.5 ampere
Current density at cathode.	$N.D._{100}$=0.5 ampere
Distance between.	Approximately 18 cm.
Material of anode.	Soft sheet lead
Material of cathode.	Soft sheet lead
Phenomenon at anode.	White lead flowing
	down in streams
Phenomenon at cathode.	Bubbling of carbon di-
	oxide gas and the
	formation of Na_2CO_3

Another plan for producing a carbonate of lead can be shown with this same piece of apparatus, but with a different electrolyte. A solution of sodium nitrate is used, which when electrolyzed forms nitric acid, which attacks the lead electrode and puts it into solution as lead nitrate. The following equations show how this scheme probably works:

1. $NaNO_3 + H_2O = NaOH + HNO_3$.
2. $2HNO_3 + Pb = Pb(NO_3)_2 + H_2$.
3. $Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$.
4. $Pb(OH)_2 + HNaCO_3 = PbCO_3 + NaOH + H_2O$.

Instead of reactions 1 and 2 taking place as shown, the following may be the true state of affairs, since hydrogen is liberated at the cathode:

$$2NaNO_3 + 2H_2O + Pb = (2NaOH + H_2) + PbO_2 + (NO_3)_2.$$

Equation 4 results from the addition to the lead hydroxide of a solution of sodium bicarbonate. Other modifications of this very beautiful method will doubtless suggest themselves to the ingenious student, apart from the interesting quantitative figures he is in a position to obtain by working with such an equipment and electrical measuring instruments. Of course, for economy in operation the motor-generator should be used, as we do not require the electric current at anything like 110 volts pressure.

Having produced the white lead, which is the basis for most oil-color paint, we can next try our hand at the electrolytic production of pigments. Perhaps the easiest and most satisfactory pigment to take up first is that of cadmium yellow.

THE ELECTROLYTIC PRODUCTION OF CADMIUM YELLOW.

This very brilliant and beautiful pigment may be easily produced electrolytically in a cell similar to that employed in the preparation of white lead. This cell is shown in Fig. 61, a cylindrical stick or rod of cadmium acting as the anode, and a strip of platinum acting as the cathode. In the place of the CO_2 generator as used in the previous preparation, a hydrogen-sulphide generator is employed. For this purpose, as is well known by every chemist, we require some fragments of iron sulphide and a little dilute hydrochloric or sulphuric acid. This generator is depicted in its simplest form, and may be replaced to advantage by one of the approved "automatic" types, whereby the supply of gas controls the action of the acid upon the iron sulphide. The electrolyte in this experiment consists of a saturated solution of common salt in water, and when electrolyzed under these conditions forms cadmium chloride at the anode, and sodium hydroxide at the platinum cathode. For the production of any quantity of this pigment, both the anode and cathode should be placed in porous pots to prevent the mixing

together of the respective electrode products. The cadmium chloride produced is immediately precipitated as the brilliant yellow cadmium sulphide by the stream of hydrogen-sulphide gas. The following simple equations indicate the steps in the production of the pigment:

$$2NaCl + 2H_2O = 2NaOH + Cl_2,$$
$$2Cd + Cl_2 + 2H_2S = 2CdS + 2HCl.$$
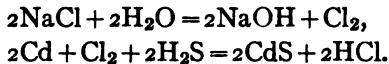
If the electrolyte is kept stirred by a mechanical device, the effect is very beautiful indeed. The tabulation of the data in the electrolytic preparation of cadmium yellow is given below:

Duration of run.................. 1 hour
Electrolyte...................... Saturated solution of NaCl in water
Character of apparatus........... See figure
Dimensions of cell............... 8 cm. $\times$ 20 cm. $\times$ 20 cm.
Source of electricity............ Lighting circuit and lamp-bank, except for economy and quantitative work. Then use motor-generator.
Temperature of electrolyte....... 30° C.
Amperes flowing................. 1.00 ampere
Volts indicated................. 4.5
Area of anode immersed.......... 50 sq. cm.
Area of cathode immersed........ 100 sq. cm.
Current density at anode......... $N.D._{100} = 2$ amperes
Current density at cathode....... $N.D._{100} = 1$ ampere
Distance between................ Approximately 18 cm.
Material of anode............... Rod or stick of cadmium.
Material of cathode............. Strip of platinum
Phenomenon at anode............ Solution of $CdCl_2$
Phenomenon at cathode.......... Liberation of hydrogen and the formation of NaOH
Phenomenon between............ The precipitation of CdS
Special peculiarities............ Use of porous pots for the production of the pure pigment in quantity to prevent mixing of electrode products.

Note here the double current density at the anode as expressed in the abbreviated manner, as the result of using a stick of cad-

mium having one-half the area of the platinum strip. The next pigment is that of mercury vermilion described as follows:

THE ELECTROLYTIC PRODUCTION OF MERCURY VERMILION.

The electrolytic production of this brilliant sulphide is a little more difficult to accomplish, as the conditions must be exactly right or the scheme does not work out as smoothly as that for the preparation of the cadmium sulphide. Fig. 62 shows the arrange-
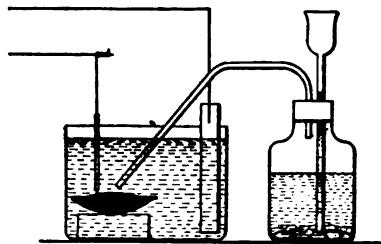
FIG. 62.—Experimental Apparatus for the Electrolytic Preparation of Mercury Vermilion from a Mercury Anode.

ment of the apparatus, where a mass of mercury acting as anode is shown within a small porcelain dish, with a strip of platinum as cathode. This little dish may rest upon a block of glass, as for example a rectangular glass paper-weight, for effect, if shown to a number of persons as a lecture experiment. A platinum wire runs down into the mercury, and is protected by a covering of thin rubber tubing to prevent its acting as an electrode. A hydrogen-sulphide generator similar to that used in the preparation of the cadmium sulphide is employed, as shown at the right. The electrolyte consists of a solution of 8 per cent each of ammonium and sodium nitrates,

$$NH_4NO_3 \text{ and } NaNO_3,$$
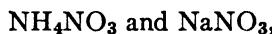
which electrolyze into NH_4OH and $NaOH$ at the cathode, and the setting free of the two corresponding NO_3 groups at the anode, which is of mercury, and consequently the soluble mercury nitrate is formed, $Hg(NO_3)_2$. The hydrogen sulphide acting upon the nitrate of mercury produces the sulphide

$$Hg(NO_3)_2 + H_2S = HgS + 2HNO_3,$$
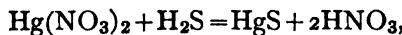
with the formation of two molecules of nitric acid, which, acting upon the ammonium and sodium hydroxides, reforms ammonium and sodium nitrate.

$$NaOH + HNO_3 = NaNO_3 + H_2O,$$
$$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$
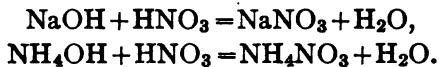
The following tabulation shows the important points to observe in the successful preparation of this vermilion electrolytically:

Duration of run................... 1 hour
Electrolyte...................... 8 grams NH$_4$NO$_3$, 8 grams NaNO$_3$ in 1 liter of water
Character of apparatus............ See figure.
Dimensions of cell............... 8 cm. × 20 cm. × 20 cm.
Source of electricity.............. Motor-generator
Temperature of electrolyte........ 50° C.
Amperes flowing................. 5 amperes
Volts indicated................... 5.5 volts
Area of anode immersed........... 200 sq. cm. approx.
Area of cathode immersed........ 100 sq. cm.
Current density at anode......... N.D.$_{100}$ = 2.5 amperes
Current density at cathode........ N.D.$_{100}$ = 5 amperes
Distance between................ 12 cm. approximately
Material of anode................ Metallic mercury (see illustration)
Material of cathode.............. Strip platinum
Phenomenon at anode............ Formation of Hg (NO$_3$)$_2$
Phenomenon at cathode.......... Production of NH$_4$OH and NaOH
Special peculiarities.............. Arrangement of mercury in small porcelain dish

For an effective lecture exhibit the vermilion sulphide should be agitated by means of a mechanical stirrer. Fig. 63 illustrates four electrolytic cells in series with electric motors attached to stirrers, producing a very striking apparatus for the simultaneous production of white lead and pigments. It is absolutely necessary to insulate the stirrer rods from the shafts of the motors if a common electric-lighting circuit and lamp-bank is employed for power for the motors and electrolyzing current. If this is not carefully done, there will, with most of the small motors on the market, be troublesome short circuits, and a failure to accomplish the electrolysis from this cause. These motors may be joined in series, and the cells

should be mounted upon a board, which may be lowered by removing the support in order to withdraw the electrodes and stirrers.
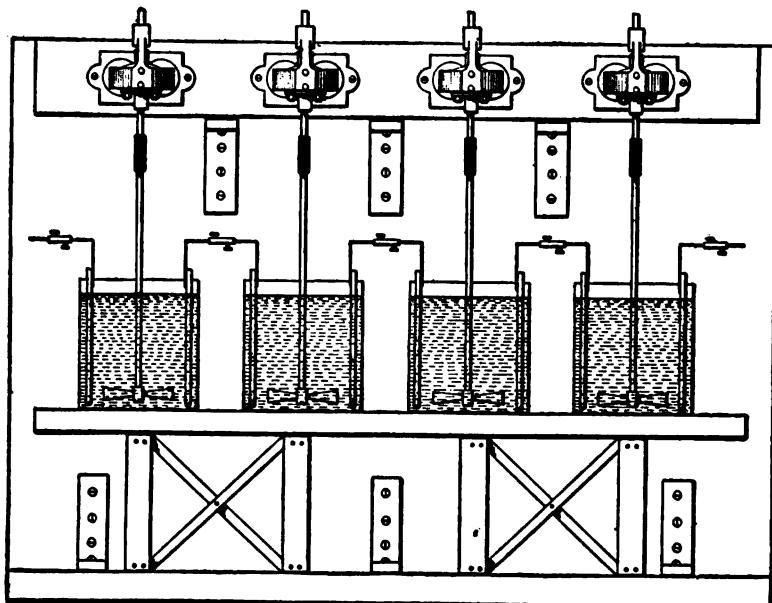
FIG. 63.—Arrangement of Electrolytic Cells with Electromechanical Stirrers for the Experimental Preparation of White Lead and Colored Pigments Simultaneously. This apparatus is designed as a striking lecture-room experiment. It is necessary to insulate the stirrer rods with hard-rubber connections as indicated in black if a common electric-lighting circuit is employed for motors and electrolysis.

It is almost needless to say that this piece of apparatus will be also useful for any other operations where mechanical agitation is required for prolonged periods of time. There are other pigments which may be easily produced in the same general manner, the details of which will be left to the ingenuity of the student. For example, a beautiful green may be produced electrolytically as follows:

THE ELECTROLYTIC PRODUCTION OF SCHEELE'S GREEN.

For this preparation dissolve 10 grams of sodium sulphate in 1 liter of distilled water and place in the electrolytic cell as employed for the previous compounds. The electrodes are cut from pure soft sheet copper about 5 centimeters by 25 centimeters for the size

of cell we are using, and about No. 18 gauge. The cell and electrolyte must be heated to a temperature of about 100° C. by means of a water-bath. A little bag of tow is made and filled with white arsenious oxide, which is suspended in the electrolyte. A current of about 3 amperes is necessary for a cell of this size, and it is better to employ the lighting current and the lamp-bank for the electrolyzing current. Copper sulphate and sodium hydroxide are formed, the sodium hydroxide dissolving the arsenious oxide and forming sodium arsenite. The sodium arsenite immediately reacts with the copper sulphate which separates as a beautiful green precipitate to form the copper arsenite, regenerating sodium sulphate. The operation may be conducted until the copper electrodes are consumed, and the arsenious oxide completely converted to the arsenite of copper.

THE ELECTROLYTIC PRODUCTION OF PRUSSIAN BLUE.

In the same general manner Prussian blue may be prepared in the electrolytic cell. A potassium ferrocyanide solution of 10 grams to the liter is precipitated by means of a normal ferrous salt solution. This precipitate is stirred in water by means of our mechanical stirrer. This must be placed in a large porous pot of sufficient diameter to admit a suitable stirrer in which a platinum anode is placed   About 25 cubic centimeters of nitric acid is added to the solution in the pot and a platinum cathode is placed outside. About 5 amperes must be passed through the system for several hours, when we will obtain for our product a dark Berlin blue.

A few words concerning experimental apparatus may be of service to the electrochemist. Fig. 64 illustrates a most convenient and satisfactory electrolytic stand for a great variety of purposes. The column is solid glass, which serves to mount the two electrode arms and effectually insulate them from each other. The electrode arms not only slide up and down the column and are set by means of a thumb-screw, but the electrodes may be slid in and out from the center of the column and set at any required distance. For rapid adjustment and flexibility of use these stands are unsurpassed. A half dozen or more of these stands should be a part of every electrolytic equipment. They are always ready to receive electrodes of various kinds and materials, and are quickly connected to the source.

of electricity by means of binding screws. Many electrochemical investigations may be begun by electrolyzing small volumes of

FIG. 64.—Convenient Electrolytic Stand for Conducting Experimental Work. The column is of solid glass, and the electrodes are easily adjusted for cells and beakers of various kinds.

electrolytes in beakers with these stands until data warranting the use of larger cells with separately fixed electrodes are secured.

CHAPTER IX.

ELECTROLYTIC PREPARATION OF POTASSIUM CHLORATE
FROM POTASSIUM CHLORIDE. PREPARATION OF SOLID
TRIOXIDE OF SULPHUR. PRODUCTION OF OZONE FROM
THE ATMOSPHERE. EXPERIMENTS WITH OZONE AND ITS
PRACTICAL APPLICATIONS.

ELECTROLYTIC PREPARATION OF POTASSIUM CHLORATE.

An outline of the purely chemical method for preparing this important compound should be given before undertaking the electrolytic plan. Potassium chlorate, or chlorate of potash, is prepared in the chemical way by passing an excess of chlorine gas rapidly into a strong solution of potassium hydroxide. When the liquid becomes hot enough to decompose the hypochlorite first formed into potassium chloride, which remains in solution, the potassium chlorate deposits in tabular crystals. The ultimate result of such a chemical method for this compound may be expressed by the following equation:

$$6KOH + Cl_6 = KClO_3 + 5KCl + 3H_2O.$$

If potassium carbonate or a weak solution of potassium hydroxide be employed, the liquid will require boiling after saturation with chlorine, in order to convert the hypochlorite into chlorate. This chemical process for the preparation of potassium chlorate is far from being economical, since five-sixths of the potash is converted into chloride, being employed merely to furnish oxygen to convert the chlorine into chloric acid. In manufacturing potassium chlorate upon a large scale, a much cheaper material is used, namely lime, to furnish the oxygen. The lime is mixed with water, and saturated with chlorine gas in closed leaden tanks, when we obtain the following reaction:

$$2Ca(OH)_2 + 4Cl = Ca(OCl)_2 + CaCl_2 + H_2O.$$
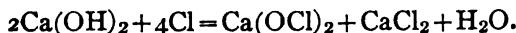
The liquid is boiled down, when the calcium hypochlorite is decomposed into calcium chlorate and chloride,

$$3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2.$$
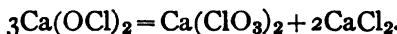
The calcium chlorate is now decomposed by boiling with potassium chloride, when it yields calcium chloride which remains in solution, and potassium chlorate which separates in crystals as the solution cools. The following equation expresses this step in the process:

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$
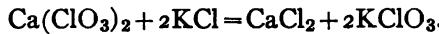
In the preparation of potassium chlora e by electrolytic means, certain difficulties are met with. The simple plan of subjecting a hot solution of potassium chloride to electrolysis, and allowing the free mixing of the chlorine and caustic soda produced, is workable only with low concentrations. To obtain the potassium chlorate f:om an electrolyte containing chloride is a rather difficult matter by means of any process of crystallizing out. Without a porous partition or means of keeping the electrode products separated, the anode or oxidized product will reach the cathode and will there be reduced. At the same time the potassium hydroxide formed at the cathode can serve independently as an electrolyte, yielding at the electrodes oxygen and hydrogen gases, with the useless expenditure of electrical energy. The student in electrochemical processes should be on the lookout for every such possibility, and should have such losses in mind in the design and construction of his apparatus. Let us take up the experimental preparation of this most important compound electrolytically in the simplest manner, using first an open beaker glass without porous partitions The student can make his determinations, and then modify the apparatus with a porous pot with a view to increasing the working efficiency. For the simplest workable plan we will employ an electrolyte of the following composition:

100 grams of potassi m chloride,
1 gram of potassium carbonate,
1 gram of potassium dichromate,
250 grams of hot distilled water.

Fig. 65 shows the arrangement of the necessary apparatus in its

simplest form. In making records of experiments in note books, it cannot be too strongly impressed upon the student to make concise and neat little sketches of the apparatus and the manner in which it was assembled, to be accompanied of course by a full tabulated list of conditions as set forth in a previous chapter. In our first illustration we have a large beaker resting upon a square of asbestos, supported by a low iron ring tripod over a special low type of Bunsen burner for maintaining the electrolyte at such an elevated temperature, as is necessary. The anode and cathode are both of sheet platinum,
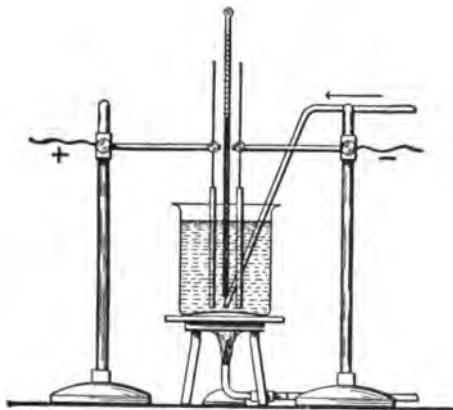
FIG. 65.—Experimental Apparatus for the Electrolytic Preparation of Potassium Chlorate from Potassium Chloride.

and are most conveniently supported by a couple of electrolytic stands with insulating glass columns, as described and recommended in the last chapter. A thermometer is immersed in the electrolyte together with a glass tube as indicated, through which a current of carbon-dioxide gas is passed. The current density at the anode should be at least 20 amperes per 100 square centimeters of immersed electrode, and the current density at the cathode should be about double this for best results. The electrolyte is kept at a temperature of 60° C. and a feeble acid reaction is maintained by a current of carbon-dioxide gas, which also keeps the solution agitated and of uniform composition. According to Dr. Karl Elbs, of the University of Giessen, at least 60 ampere hours are necessary for this quantity of electrolyte, since one ampere hour yields 0.75 gram of potassium chlorate. According to Dr. Elbs, if a separation of potassium chlorate has

commenced during the electrolysis, after allowing the electrolyte to cool down, a considerable quantity of potassium chlorate crystallizes out, which is purified by a single recrystallization. By evaporation of the mother liquor to about one-half its original volume and then allowing it to cool down, a second lot of crystals is obtained. The current efficiency amounts to about 70 per cent of the theoretical, and only begins to fall off to a serious extent if over 50 per cent of the potassium chloride has been converted into potassium chlorate. It is very evident from the foregoing that if the current efficiency be calculated from the amount of potassium chlorate in the crystalline solid form, the figure obtained will be too low because of the quantity remaining behind in the mother liquor. Sodium chlorate may be prepared with the same apparatus by using as an electrolyte,

FIG. 66.—Useful Design of U Tube for Conducting Electrolytic Preparations and Maintaining an Elevated Temperature by the Current Itself. The center tube receives the thermometer.

> 80 grams of sodium chloride,
> 2 grams of sodium carbonate,
> 1 gram of sodium dichromate,
> 250 grams of hot distilled water.

The electrical conditions are the same as in the preparation of potassium chlorate and the current efficiency is also about 70 per cent. The electrolyte in this case is evaporated to a small volume, when the sodium chloride will separate out of the solution and is filtered off. The final product is not pure, being contaminated with sodium chloride and sodium chromate. Sodium chromate is exceedingly soluble, and a complete purification is therefore a difficult matter.

Potassium and sodium chlorates may be quickly prepared in small quantities without the aid of external heating by employing a special U tube with a center limb like that illustrated in Fig. 66. Because of the comparatively small cross-section of the electrolyte, the temperature can easily be kept at the required point by controlling the electric

current.   The central tube serves for the reception of the thermometer. Such a piece of apparatus not only serves for this particular line of electrolytic work, but is of a generally useful and flexible character. **Fig.** 67 illustrates such a tube in connection with an ammeter and
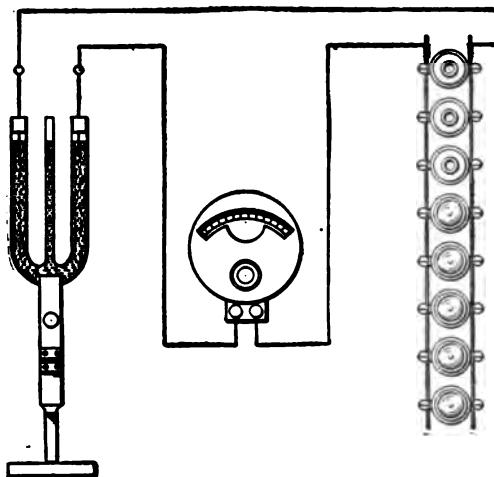
FIG. 67.—Combination of Special U Tube with Ammeter and Lamp-bank, where-by Electrolytes can be Maintained at their Boiling-points by the Electrolyzing Current. By means of the ammeter and the thermometer conditions can be easily controlled.

lamp-bank, by means of which electrolytes can easily be maintained at their boiling-points by the electrolyzing current if necessary.

PREPARATION OF SOLID TRIOXIDE OF SULPHUR.

It will be remembered that in a previous chapter the electrolysis of concentrated sulphuric acid was conducted with the liberation of hydrogen, oxygen, ozone, and free sulphur, and at elevated tempera-tures the electrode products become hydrogen, oxygen, and sulphur trioxide. If now we select a thin glass Woulf bottle intended for heat-ing, and subject concentrated sulphuric acid to a process of electrolysis with a heavy current, we will elevate the temperature sufficiently to produce sulphur dioxide in quantity, which may be condensed to a white solid with ease by passing the gas into a suitable condenser. This experiment is not intended to show a method for preparing sulphur trioxide, to compete with any existing chemical schemes,

but merely as an exercise of interest in conducting practical work. Fig. 68 shows the arrangement of the apparatus, which consists of a thin Woulf bottle with platinum electrodes and a thermometer for noting the temperature.   There is a glass tube leading to a condenser fitted with stop-cocks immersed in a freezing-mixture, and a lamp-bank for modifying the lighting current.   Electrical measuring instruments are shown in this illustration, although the production of this interesting compound upon this plan hardly warrants the setting down of efficiency data.   Like the experiment with the cold acid,
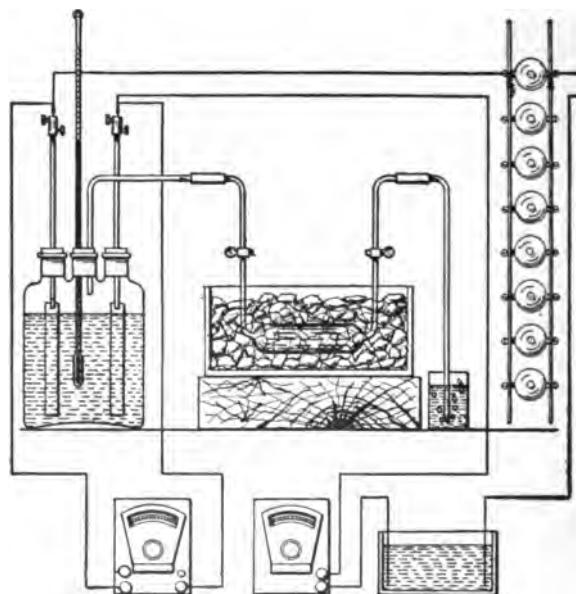
FIG. 68.—Experimental Preparation of Solid Sulphur Trioxide by the Electrolysis of Concentrated Sulphuric Acid.

the experiment is useful in demonstrating the composition of sulphuric acid by electrolytic means.   Such a piece of apparatus is very useful in conducting research work upon compounds when the mechanism of electrolysis is doubtful.   For example, in electrolysis we may be obtaining a condensible gas from one of the electrodes, and it would be highly desirable to obtain this gas in a liquid or a solid form for identification.   In a certain piece of research work undertaken by the author, oxides of nitrogen were given off on electrolysis, and it was convenient to pass the electrode gas through such a condenser immersed in liquid air, when the oxides of nitrogen con-

densed to a light-blue solid, and were estimated in this form. Sulphur dioxide, as is well known by all general chemists, can be liquefied by passing it through such a condenser immersed in a simple freezing-mixture of ice and salt. It is believed that, apart from introducing an experiment, or a method of preparing a compound, the description of special and useful apparatus will prove as valuable to the experimenter and investigator as many theories and their applications. Having produced a number of typical electrolytic preparations in inorganic chemistry, we would neglect some very important applications of electricity to chemistry, unless we prepared certain important gases of commercial value. Perhaps the first gaseous preparation should be that of ozone, and the following pages will therefore be devoted to this valuable product.

THE ELECTRICAL PRODUCTION OF OZONE.

Ozone is the chemical name applied to a peculiar form of oxygen the exact nature of which is open to some little discussion, as it has been impossible to obtain absolutely pure ozone. It is always accompanied with ordinary oxygen, but there are good reasons for believing that ozone consists of three atoms of oxygen. Three atoms of oxygen, occupying three volumes, therefore, combine to one molecule of ozone which occupies two volumes. Ozone, according to this scheme of formation, would be one-half as heavy again as ordinary oxygen, and experiments upon its rate of diffusion go to support this theory. In the year 1785, Von Marum noticed that oxygen upon being subjected to electrical discharges, acquired an odor like that experienced after the atmosphere had been subjected to an active electrical storm. In 1840, Schoenbein called attention to the similarity between the odors produced when air was treated to electrical discharges, and the odors noticed when water was electrolyzed between platinum electrodes, or gold electrodes, for with the baser metals the production of ozone was not so marked. The
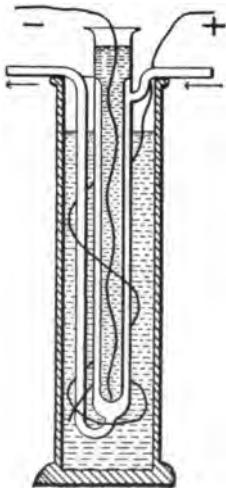
FIG. 69. — Experimental Apparatus for the Production of Ozone from the Atmosphere. Dilute sulphuric acid fills both outside cylinder and inner chamber of the central tube.

production of ozone was probably just as great, only it was largely expended in oxidizing the electrodes when they were not of platinum or of gold. The same investigator also observed that a like odor accompanied the slow oxidation of phosphorus, and also of sulphur, and that in each case a piece of filter-paper moistened with a solution of starch and potassium iodide was turned blue. About the same time, two other investigators, Marignac and De la Rive, showed that ozone was only a changed condition of oxygen. In 1852, Becquerel and Fremy demonstrated that pure oxygen could be converted into ozone. In 1860, Andrews and Tait called attention to the fact that a marked contraction in volume accompanied the formation of ozone from oxygen, and in the same year Soret showed that oil of turpentine absorbed ozone completely, and in this way determined its relative density, confirming his results in 1867 by the method based on the rate of the diffusion of gases as already mentioned. Andrews suggested at this time that the substance present in the atmosphere which affected starch and potassium iodide paper was this modified form of oxygen. We have already seen that ozone may be obtained in the electrolysis of concentrated sulphuric acid between platinum electrodes. Is this the most efficient and economical way of producing it? It is not, for there have been designed and put into practice many forms of special ozone-generators of greater efficiency. For laboratory purposes the generator as illustrated in Fig. 69 has proven very useful. Here the apparatus is shown in section in order that its several parts and their relations may be clearly seen and understood. The tall outside cylinder glass is filled with dilute sulphuric acid, one to ten, as well as the inner chamber of the tube which is immersed therein. Two platinum wires are dipped respectively into the acid in the outer glass cylinder, and in the acid in the inner tube. When these platinum wires are connected to the secondary terminals of a good induction-coil, the two portions of the sulphuric acid become electrified, and there is believed to be a stress set up which resolves the oxygen molecules into its atoms, with a recombination to form molecules of ozone. Dry air or dry oxygen is passed through the space between the two portions of acid, which space for most economical action should be as narrow as possible. Another important condition is the temperature of the air or oxygen used. It should be cooled down to a

low temperature before sending through, and should not be supplied too fast. Fig. 70 illustrates a special horizontal form of ozone ap-

FIG. 70.—Another Form of Ozone Apparatus Based upon the Same Principle. The outer and inner tubes contain dilute sulphuric acid. The inner tube is sealed up, only a small air-bubble remaining.

paratus based upon the same general principle. The longer the tube and the greater the area exposed to the oxygen or air the greater the ozonizing power of the apparatus for a stream of air or oxygen of a given velocity and volume. The ordinary chemical test for ozone, as has been intimated, is a damp mixture of starch and potassium iodide, preferably made into test-paper. To make a good test-paper for our work with ozone preparation, take 100 grams of starch and grind thoroughly in a mortar with 50 cubic centimeters of distilled water. The thin paste is then poured into 250 cubic centimeters of boiling distilled water in a beaker, and one-half a gram of potassium iodide crystals are added and made to dissolve by stirring. Narrow pieces of filter-paper are drawn through this solution with glass rods and hung up to dry. When these pieces of paper are moistened, and exposed to ozone, they turn blue, but are not affected by ordinary oxygen. The ozone abstracts the potassium from the potassium iodide, and sets free the iodine, which has the specific property of imparting a deep-blue color to starch. Papers impregnated with manganese sulphate, lead acetate, or thallous oxide, become brown, in the first two cases by the formation of the peroxide of the metal, and in the last case from the formation of thallic oxide, under the influence of ozone. Thus it will be seen that ozone is an excellent and energetic oxidizing agent. If ozone is passed into a solution of indigo, the blue color will soon disappear, since the ozone oxidizes the indigo, and gives rise to products which, in a diluted state, are nearly colorless. Ordinary oxygen is not capable of bleaching indigo in this manner. If ozone is passed through a tube of vulcanized caoutchouc, this will soon be perforated by the

corrosive effect of the gas, while ordinary oxygen would be without
effect upon it. If ozonized air be passed into a flask with a little
mercury in the bottom, the surface of the mercury will soon be
tarnished as the result of the formation of oxide, and when the mercury
is shaken around in the flask, it will adhere to the sides, which will
not be the case with pure mercury, as is well known. Let us look
into other forms of ozone apparatus and the application of the
electricity. Fig. 71 illustrates a simple Siemens tube, which is
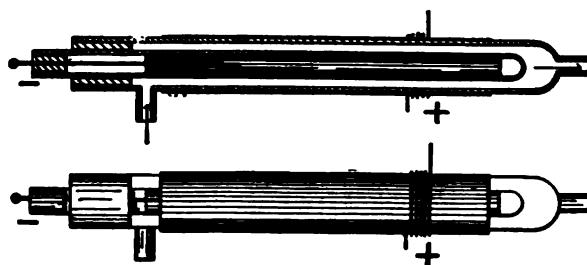
FIG. 71.—Cross-section and Elevation of an Original Siemens Apparatus for the
Production of Ozone from Atmospheric Oxygen. The sulphuric acid is dis-
placed in this tube by some metal not readily oxidized, such as tinfoil.

perhaps the simplest to construct in the laboratory. Here we have
merely an inner and an outer tube as shown in the sectional view.
The inner tube is held in position by a good cork and is lined on
the inside with tinfoil. This tube is closed at one end by sealing
off, and at the other end by a cork stopper through which a platinum
wire passes and makes contact with the tinfoil lining. The outer
tube has a side and end tubulure through which the air or oxygen
gas is passed. This outer tube is coated with tinfoil on the outside
with which electrical connection is also made. A good induction-
coil with a condenser of large capacity is employed with this apparatus
as with the acid tubes. In a lecture by Froelich he has given an
account of the experiments which have been made in the laboratory
of Messrs. Siemens & Halske in Berlin for the commercial production
of ozone. The original Siemens ozonizing tube was like that
illustrated, the two coatings being supplied with an alternating
current of high potential, while oxygen was made to traverse the
annular space between the two tubes. It appears that only one
dielectric is necessary, mica, celluloid, porcelain. and the like being

available, as well as glass, and the ozone tube having either a metal tube within and a metal-coated non-conducting tube without, or a · metal tube without, while the inner tube is made of the non-conducting material and lined with metal. The metals to be used are of course those which are not attacked by ozone, such as platinum, tin, or aluminium. Cold water flows through the inner tube, and through the annular space pure, dry air. Several such tubes may of course be combined into one system and be worked equally well with the alternating currents, although for single tubes it is stated that direct currents operated by interrupters may be used to advantage. The apparatus as described by Froelich in the German laboratory yields 2.4 milligrams of ozone per second. Experiments have been made with a view of producing compressed ozone for technical uses, this having already been done on a small scale under a pressure of about 10 atmospheres. One use of ozone especially dwelt upon by Froelich is the oxidation of organic impurities in drinking-water. Experiments with ozone upon water-supplies have been made in this country, nevertheless, for a long time. In all productions of ozone it is very important to keep the temperature low, and the following experiment will serve to impress this fact upon the student: If ozone be made to pass slowly through a glass tube heated in the center by a Bunsen burner, it will be found to lose its power of affecting starch and potassium iodide paper, the ozone having been reconverted into ordinary oxygen under the influence of heat. The formation of ozone may be compared with the production of hydrogen peroxide, and we may express this breaking up of ozone symbolically. Just as hydrogen dioxide, H_2O_2, may be regarded as formed by the combination of a molecule of water H_2O, with an atom of oxygen, so ozone may be viewed as a combination of a molecule of oxygen O_2, with an atom of oxygen. The breaking up by heat of ozone may, therefore, be expressed,

$$2(OO_2) = 3(O_2).$$

A temperature of 250° C. is sufficient to completely bring about this breaking up of the ozone. As we have learned, a given volume of oxygen diminishes when a portion of it is converted into ozone by the silent electrical discharge, and it regains its original volume

when the ozone is reconverted by heat. It is of interest to note that the conversion of oxygen into ozone is attended by the absorption of heat; in other words, it is endothermic. The value of this heat absorption may be expressed thus:

$$3O_2 = 2O_3 - 59,200 \text{ calories.}$$
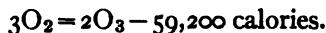
Ozone is, therefore, a very unstable body theoretically, and practically we find such a state to be the case. To work any one of the ozonizers economically in the laboratory the author has found it very convenient and satisfactory to first dry the oxygen or air by passing it through concentrated sulphuric acid, and then through a long tin or lead worm immersed in iced water. Chilled, dry oxygen of course gives the richest yield of ozone. A very efficient design of ozone-generator and one of easy manufacture in the laboratory is illustrated in connection with an induction-coil in Fig. 72. This simply consists of a large outer glass tube of any length, containing a number of small thin-walled glass tubes closed by sealing off at one end. Narrow strips of tinfoil are pushed into each tube, as indicated, and joined together in the manner of connecting up an electrical condenser. A stream of chilled, dry air or oxygen is passed through the large tube. Of course for a large outer tube of great length a very powerful induction-coil must be employed. The adjustment of the size and length of tube to the induction-coil, the temperature, dryness and rate of supply of air or oxygen, etc., make a very valuable set of conditions for the student to experiment with with a view to obtaining a combination for maximum efficiency. The electrical energy supplied to the coil should of course be measured, as well as every other chargeable item in the production of the body in question. There are other ways of producing ozone electrically, although in point of efficiency they cannot be compared with those described. Among the experiments in electrolysis yielding as one of the products ozone, may be mentioned the electrolysis of aqueous solutions of nitric acid, hydrofluoric acid, sulphuric acid, and phosphoric acid, as well as solutions of potassium nitrate, potassium phosphate, and sodium sulphate. Hydrochloric, hydrobromic, or strong nitric acid do not produce ozone when electrolyzed. Neither do aqueous solutions of metallic chlorides, bromides, iodides, or ferrous sulphate.

According to Houzean, the electrolysis of water furnishes only 3 to 5 milligrams of ozone per liter. When a given quantity of oxygen is subjected to the action of charged surfaces, as presented in any of the foregoing descriptions of ozonizers, only one-fifth, at most, according to Bloxam, is converted into ozone; but if the ozone be now removed by some substance which absorbs it, a fresh quantity of the oxygen may be ozonized. The proportion of ozone formed depends upon many conditions, the intensity and frequency of the
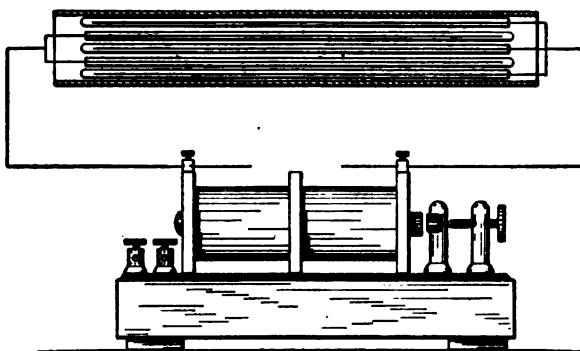
FIG. 72.—Efficient Type of Ozone Apparatus and Induction-coil Assembled for Production.

electrical discharge, the pressure, quantity, temperature, etc. The question of temperature in all ozone processes appears to be by far the most important. According to the older researches, about the time 1880, 20 per cent of the oxygen becomes ozone at $-25°$ C., and only 12 per cent at 20° C., the ordinary working temperature of a chemical laboratory. At the temperature of boiling water, the production is but 2 per cent. In more recently made determinations, 1893, it is stated that the production is 5.2 per cent at 20° C. The matter of ozone production has occupied the minds of many inventors during the last few years, and many forms of commercial apparatus have been designed and constructed to produce this gas upon a very large scale. There are drum-shaped chambers containing many sets of stationary tinsel brushes arranged around the cylindrical interior, with corresponding revolving sets of brushes to constitute the opposite pole, for example. High potential discharges of varying current strength have been experimented with in such pieces of

apparatus, and it has been found, to produce the best effects, that high potential difference with small current and energy value must be used. Probably this is due to the absence of heating effect with electrical discharges of small quantity. A thick, heavy discharge appears to break up the ozone formed almost as rapidly as it is produced.

COMMERCIAL PRODUCTION OF OZONE AND ITS APPLICATIONS.

Among the early plants for the commercial production of ozone for its practical application may be mentioned two equipments in Germany, where ozone is used as a sterilizing and oxidizing agent in connection with commercial water-works and supplies. These plants are situated in Schierstein, near Wiesbaden, and in Paderborn respectively. Ozone is well adapted for water sterilization and purification, being a powerful destructive agent to all organic matter both animal and vegetable. Of its efficiency there is no longer any doubt, as experiments conducted over a long space of time all go to prove its great efficiency. The question lies in the cost entirely, and in order to secure figures of value upon this question we must study a commercial working equipment. The two German plants referred to were installed by the Siemens & Halske Company, of Berlin. The plant at Schierstein is designed to sterilize 66,000 gallons of water per hour as a maximum. This maximum output is called for only on occasions when exceptionally large quantities of water are required, while the average demands are about one-half of this, or 33,000 gallons per hour. This plant is divided into two independent units, like lighting and power units, the one being in opera‧tion while the other is at rest. The electrical generators installed furnish electricity for operating pumps for the air and water, and also for working the step-up transformers. These transformers receive the current at a pressure of 120 volts and supply a current from the secondary winding, at a pressure of 8,000 volts, the secondaries of course being connected with the ozone-generators. The ozone produced by the action of this discharge is driven by fans into the sterilizing-towers, in which the ozone rises and comes in contact with the water flowing down. The water is thus intimately mixed up with the gas, and is thereby purified and flows off to a reservoir.

In the ozonizer-room there are 48 ozone-generators mounted on stout shelves on both walls opposite an aisle, the battery being divided into two halves to be connected with the two generating units respectively. Each half, therefore, contains 24 ozone producers or generators, and these in turn are divided into three series, of 8 ozonizers each, and each series of eight is connected to the 8000-volt secondary winding independently. We have, therefore, three sets of 8 ozonizers in series, connected in parallel to the secondary of the transformer. One series of 8 ozone-generators produces a sufficient quantity of ozone for one sterilization-tower. The ozonizers are of the Siemens-tube type, constructed of glass and metal, one pole being grounded on account of the method employed of cooling the inner tube with water. The connections to the positive pole, the pole which is not grounded, are well protected, so that it is not possible for the attendants to meet with accidents from the high potential. Eight ozonizing tubes or generators are contained in an iron box, the upper, lower, and front sides of which are provided with heavy glass windows. The ozonizer-room is usually kept darkened, and the attendant whose duty it is to enter it sees at once from the blue light passing through the glass windows of the apparatus whether it is working satisfactorily or not. As all the metallic parts connected to the 8000-volt poles are carefully protected on the one hand, and grounded on the other, there is little danger of a fatal accident. The sterilizing-room in this plant contains two series, each of four towers, of brick. Each tower is divided into four sections by two partition walls perpendicular to one another. These towers are filled with a coarse gravel through which the water trickles on its downward flow, presenting a great surface to the action of the ascending ozone. Through the combined four sections of each tower, 11,100 gallons of water are flowing downward per hour, while in the same time 2800 cubic feet of ozonized air pass upward through the gravel. For the operation of each half of the plant, sterilizing 33,000 gallons of water per hour, 50 horse-power are required, of which 27 horse-power are used for the ozonizers, 22 horse-power for the pumps, and 1 horse-power for various minor purposes. The cost of the process at Schierstein is 0.35 cent per cubic meter of water sterilized, 0.1 cent. being the cost of the coal required for the operation of the ozonizing apparatus. To this

must of course be added the usual interest on the money invested in the plant, and the cost of depreciation and repairs. This particular plant has to operate pumps in addition to its electrical apparatus, which is very unusual, and can be deducted from the cost in almost any other water-works. Tests of the sterilized water, made by leading German chemists and bacteriologists, proved that the sterilization process by means of this apparatus is in every way successful so far as the annihilation of germs and bacteria is concerned. The process has therefore been shown to be well adapted to the purification of drinking-water. The installation at Paderborn is similar to that at Schierstein, with the exception of the sterilizing-towers. The purified water in this plant is allowed to flow off in the form of a cascade, in order that the contained ozone dissolved may be liberated and given off. The cost of purifying a cubic meter of water in this equipment is placed at 0.4 cent, including interest, depreciation, wages, etc.

Apparatus has been designed, and constructed, and tested at Niagara Falls in this country, using an electrical discharge under a potential difference of 50,000 volts against the 8000 employed at the German works. Ozone produced with this equipment was passed through two pipes to a water-sterilizing-tower partly filled with broken rock, one supply-pipe entering the bottom and the other the top of the tower. The water flowing through the tower downward meets with the gas from all sides, above and below, and is purified by its contact with the several ozone streams. It is claimed that 30 to 40 horse-power are sufficient to sterilize 6000 tons of water daily. Some interesting experiments have been conducted by Warburg, who investigated the production of ozone by discharges in a closed volume of oxygen. In this case the formation of ozone has a limit which varies widely with the conditions of the experiment. Besides the ozonizing effect of the electrical discharges, there exists also a contrary effect which counterbalances the production after a time. Since for the limited duration of the ozonizing process the spontaneous decomposition of the ozone is negligible, it follows that the electric discharge itself must produce the contrary effect. In endeavoring to obtain a measure of both effects, Warburg starts from the assumption that the ozonizing effect is proportional to the number of molecules of oxygen present, while the decomposition

is proportional to the number of ozone molecules present.   There is a decided difference between the behavior of a positive discharge and that of a negative discharge; the maximum percentage of ozone produced, according to Warburg, is about three times as high for negative as it is for positive discharges.   If after the negative maximum is reached, the mixture is subjected to the positive discharge the percentage falls to the positive maximum.   The decomposing activity is the same for positive and negative electricity, but the ozonizing action itself is three times higher for negative electricity.   The effect of temperature upon both discharges is the same.   The author has not verified these data, but introduces them as the work of a careful and reliable experimenter.   If partly ozonized oxygen is left to itself, the proportion of ozone decreases, according to Warburg, in an interesting manner for different conditions.   This decrease is known under the name of spontaneous deozonization, and may be due to a great variety of causes.   The experimenter referred to points out that since the amount of ozone at 200° C. in a state of equilibrium is inappreciable, such equilibrium can be attained at ordinary temperatures only by complete dissociation of the ozone. The factors bringing about this dissociation may be external, as for instance, a contact with foreign bodies or with the walls of the vessel; or they may be internal and due to the collision of two molecules of ozone, or of a molecule of ozone with a molecule of oxygen.   Warburg formulates a mathematical theory of the process, and finds by suitable experiments that the internal effects are almost entirely due to collisions between the ozone molecules themselves. Heat increases this internal disintegration much more rapidly than it does the external process, and it becomes the chief agent at high temperatures.   The experimenter in question finds that moisture makes no difference in the stability of ozone at 100°.   The various forms of ozone-generators suggested and in use to-day would fill a volume in themselves, and it is believed that the fundamental principles and typical forms introduced here will be a sufficient guide to the student who wishes to experiment with this interesting and valuable modified condition of oxygen.   In the next chapter another gaseous product will be dealt with of no less scientific interest or technical value.   This will pertain to the electrical production of nitric acid from the atmosphere.

CHAPTER X.

THE PRODUCTION OF NITRIC ACID FROM THE ATMOSPHERE WITH HISTORICAL NOTES.

WE know, as general chemists, that nitric acid is one of the most important of all chemical compounds, and that it is usually obtained from potassium nitrate, which is obtained as an incrustation upon the surface of the soil in hot and dry climates, as in certain parts of India and Peru. The salt imported for the chemical production of nitric acid from Bengal and Oude consists of potassium nitrate, while the Peruvian or Chilian saltpeter is sodium nitrate. Either of these nitrates serve for the production of this important acid. On a small scale in the laboratory, nitric acid is prepared by the distillation of sodium or potassium nitrate with an equal quantity by weight of concentrated sulphuric acid. The decomposition of potassium nitrate by an equal weight of sulphuric acid is represented by the following chemical equation:

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4.$$
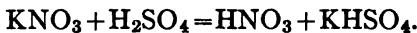
It would appear from a study of this equation that one-half of the sulphuric acid might be saved, inasmuch as one molecule could be made to decompose two molecules of potassium nitrate as follows:

$$2KNO_3 + H_2SO_4 = 2HNO_3 + K_2SO_4,$$
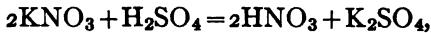
but it is found that when a smaller quantity of the sulphuric acid is used a very much higher temperature is necessary to bring about the complete breaking up of the saltpeter, and that much of the nitric acid is decomposed, and the normal potassium sulphate, K_2SO_4, which is the final result, is much more troublesome to get into solution in order to remove it from the retort or still. For the prepara-tion of large quantities of nitric acid sodium nitrate is used instead

of the more costly potassium nitrate. The chemical production of nitric acid dates back to very early times. Geber, the old Arabian alchemist, produced this acid by distilling saltpeter, copper vitriol, and alum. As early as the thirteenth century, Raymund Lullius described its preparation by distilling saltpeter with iron vitriol. Glauber, in the seventeenth century, produced it by the same method as is employed to-day, that is by the distillation of potassium or sodium nitrate with sulphuric acid. Cavendish, in his studies of the atmosphere, showed that it consisted of a mixture of oxygen and nitrogen. Although these elements in their pure condition show no attraction for each other, five distinct compounds of oxygen and nitrogen are prepared in various indirect ways. These compounds, which should be familiar to all of us who have given attention to general inorganic chemistry, are as follows:

N_2O, nitrous oxide;
NO, nitric oxide;
N_2O_3, nitrogen trioxide;
NO_2, nitrogen peroxide;
N_2O_5, nitrogen pentoxide.

When a succession of powerful electric sparks were made to pass through dry air in a flask, a red gas, NO_2, nitrogen peroxide, was formed, and when these discharges were allowed to take place in the presence of moisture, this gas was absorbed and converted into a mixture of nitrous and nitric acids,

$$2NO_2 + H_2O = HNO_2 + HNO_3.$$

If instead of water we place in the flask a weak solution of potassium hydroxide, instead of obtaining the mixed acids, we obtain the two salts, potassium nitrite, and potassium nitrate:

$$HNO_2 + KOH = KNO_2 + H_2O,$$
$$HNO_3 + KOH = KNO_3 + H_2O.$$
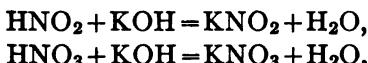
By evaporating to dryness such a solution, we obtain a saltpeter consisting of potassium nitrite and potassium nitrate, and if we distill this product with strong sulphuric acid we will obtain nitric acid. Cavendish went through this process and prepared the above

compounds without difficulty. If the experiment of passing sparks
through air (for best effects the air should be mixed with some pure
oxygen) be repeated in a U tube having one of the vertical limbs
of the tube provided with a stoppered globe into which the two
sparking wires are sealed, and we fill this system, all but the globe,
with water colored blue with litmus, the solution will be reddened
by the acids formed, and the air in the globe will be found to diminish
in volume.   Fig. 73 shows this form of "U " tube and the arrange-
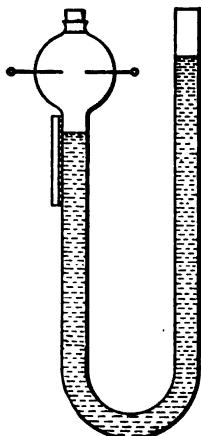
FIG. 73.—Special Form of U Tube for Showing Absorption of the Oxides of Nitrogen
by Water.

ment of the experiment.   The blue litmus solution is placed in the
tube with the stopper in place so that we will have a difference in levels
as indicated in the illustration.   A little scale, as shown at the left,
assists us in determining the diminution in volume when the oxides
of nitrogen combine with the contained water.   This formation of
oxides of nitrogen may be regarded as the combustion of nitrogen in
oxygen due to the kindling effect of the electric spark.   A simple non-
electrical experiment to illustrate the probable combustion of nitrogen
in oxygen may be performed by igniting a piece of magnesium ribbon
in a tall glass jar of carefully dried air.   If such an experiment be
performed and one looks down into the jar red fumes may be seen
and the presence of oxides of nitrogen may be shown by drawing the
contents of the jar through a mixture of potassium iodide with starch
and acetic acid, when the iodine will be set free, which blues the

starch. This experiment makes it appear likely that the electric spark causes the combustion of nitrogen in oxygen on account of a kindling effect. When ozonized air is passed into water nitric acid is found in solution. It has also been shown that rain-water contains about one part per million of nitric acid. When hydrogen gas, mixed with a small quantity of nitrogen, is burned, the water collected as the result of the combustion is found to be slightly acid, due to the presence of some nitric acid, due to the combination of the nitrogen with the oxygen of the air under the high temperature of the burning hydrogen. With the recording and appreciation of such experiments a new method of preparing nitric acid began to dawn upon chemists in general. In the year 1859, Newton produced nitric acid from the atmosphere by constructing a modified form of U tube and bulb, differing from that already illustrated only in the shape of the chamber. Newton employed a more spacious design of chamber for the air and water into which he inserted his sparking wires. Means were provided in this chamber for sending in a fresh supply of air and for allowing the acidulated water produced to run off. Prim, in 1882, modified this arrangement and used both a silent electrical discharge and a series of sparks to bring about the combination of the nitrogen with the oxygen present in a chamber. In the year 1892 Sir William Crooks produced what he termed an electric flame, through the agency of a high voltage alternating electric current discharge between pieces of platinum, and by its means brought about the combustion of nitrogen in oxygen. Lord Rayleigh and Professor Ramsay employed such a flaming arc in a number of their researches upon the atmosphere in connection with the oxidation of nitrogen. They employed an alternating current stepped up to a difference of potential of 8000 volts. Lord Rayleigh in his work upon the production of nitric acid from the atmosphere employed a spherical glass chamber with a capacity of about 50 liters in which could be maintained a fountain of sodium or potassium hydroxide solution. Into this chamber air and oxygen were slowly pumped containing a flaming discharge between platinum terminals. It is stated that Lord Rayleigh produced with this equipment about 40 grams of nitric acid per hour with the expenditure of about one electrical horse-power in energy. McDougall and Howles describe an equipment for producing nitric acid from the atmosphere, and its per-

formance, which is of special interest to the student in this line of work. They outline an alternating current-generator with a frequency of 60, equipped with two separate armature circuits. One of these windings delivers a current of 24 amperes at 200 volts pressure, and the other 12 amperes at 400 volts pressure. The current of this alternator, from either winding at will, can be led to
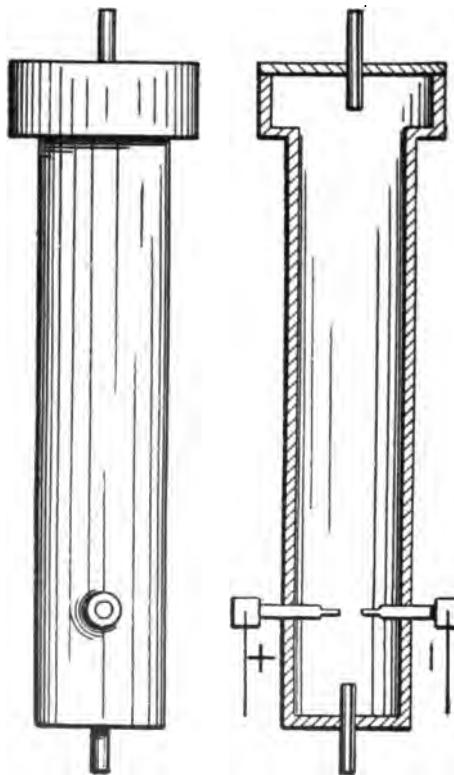
FIG. 74.—Stone-ware Pipe used as Combustion Chamber for Producing Nitric Acid from Atmosphere.

a step-up transformer with a ratio of 1 to 40, so it will be seen that a voltage at the secondary winding of the transformer of either 8000 or 16,000 volts may be obtained. The current in the primary of the transformer may be very closely measured by inserting an ammeter, and through the agency of a voltmeter at the terminal of the alternator the initial electrical pressure can be recorded. A

wattmeter was also included in the primary circuit by means of which the readings of the voltmeter and the ammeter could be checked and the energy consumed in the flaming discharge could be ascertained. An early form of combustion chamber equipped with platinum-iridium electrodes for the production of nitric acid from the atmosphere with this electrical equipment, consisted of a stoneware pipe of the shape depicted in Fig. 74. Air is drawn through this chamber during the time of an electrical discharge, and the oxidized nitrogen is drawn through a series of Woulf bottles containing either water, or a solution of sodium hydroxide. Instead of employing the Woulf bottles a series of towers may be employed to great advantage, each tower containing broken glass for the
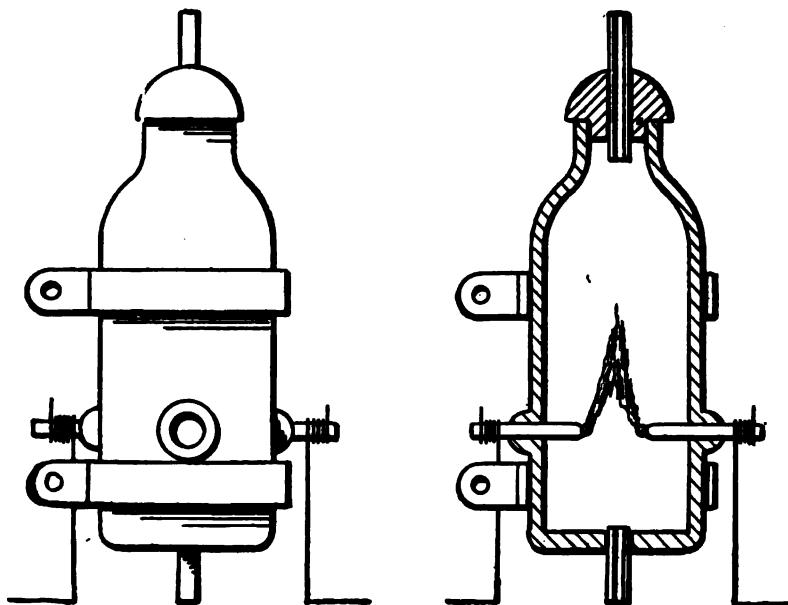
FIG. 75.—Modified Form of Combustion Chamber for the Production of Nitric Acid.

water to run over and cause it to present a great surface for absorption to the oxides of nitrogen which are made to pass through. We can produce a solution of sodium nitrate, or free acid, at will with this equipment. The form of the combustion chamber itself underwent numerous evolutions, one or two of the shapes being given here as a matter of interest and guide to the student. Fig. 75 shows one

of these modifications.   This chamber consists of a large stoneware
bottle with vertical supply and outlet tubes for the gases.   Lord
Rayleigh showed that these combustion chambers should be quite
spacious; in other words, that there should be a considerable amount
of room about the flaming discharge.   If the air is not passed through
at a certain maximum rate, the oxides of nitrogen formed will be
broken up again by the discharge, very much like the behavior of
ozone when subjected to heat after its formation.   The oxides of
nitrogen should be removed from the field, or influence of the arc as
soon as possible for high efficiency in yield.   A too rapid supply of
air causes the electrical discharge to become unsteady, and a loss in
efficiency results.   Some interesting and valuable data were obtained
on nitric acid from air by McDougall and Howles using various
forms of combustion chambers, and supplying the electricity under
different conditions.   Fig. 76 is another form of combustion chamber
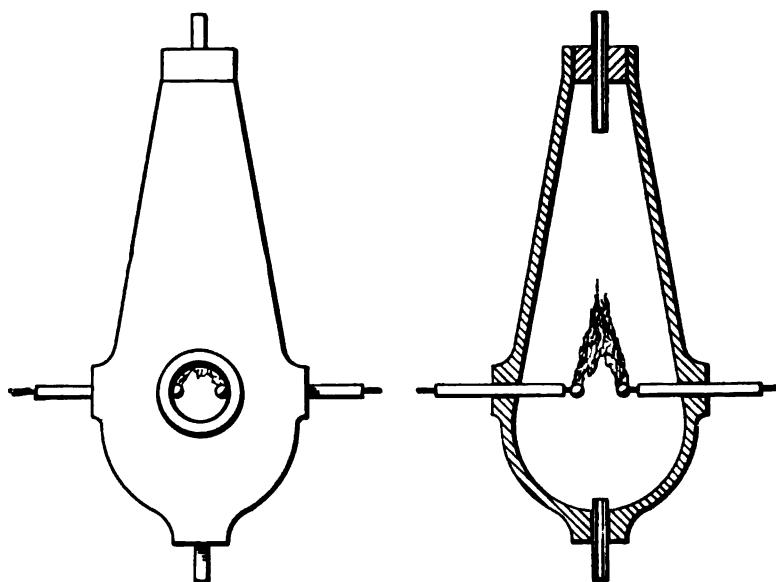
FIG. 76.—Another Modification of Combustion Chamber.

as described in the work of these experimenters.   They varied the
forms and sizes of the chambers, keeping the electrical conditions
constant, and kept the forms of combustion chambers constant,

and varied the character of the electrical discharges, making quantitative determinations of the nitric acid obtained in each case. By varying the current value in the secondary circuit of the transformer, keeping the voltage constant, these experimenters were able to vary the temperature of the flaming discharge, and to study its effect upon the yield of nitric acid produced. They formulated the following table which brings out the fact that a high temperature discharge is unfavorable to high efficiency, and consequently we can produce more acid with a fewer number of watts, or, in other words, with less electrical horse-power.

Watts Used in Flame.	Current Used in Flame.	Yield of Acid per H.P. per 12 Hours.
302	.3 to .38 ampere	180 grams
225	.2 " .25 "	270 "
172	.15 " .2 "	300 "

Too great a decrease in the current value of the flame caused the flaming arc to become unsteady and liable to extinction. The production of nitric acid by these experimenters with the foregoing electrical equipment and design of chambers, at the rate of 300 grams of nitric acid per horse-power for twelve hours, represents 51.5 per cent of the amount theoretically obtainable from the amount of air supplied. This result compares very favorably with the figures obtained by Lord Rayleigh, working with a mixture of oxygen and nitrogen in the proportion of two volumes of oxygen to one volume of nitrogen, when he obtained 440 grams of nitric acid in the same time and with the same consumption of electrical energy. When ordinary air is used in these chambers, the theoretical proportions of oxygen and nitrogen for the production of the oxide are diluted with an excess of nitrogen, which of course is detrimental to the best effects. An experiment was conducted in one of these chambers with a mixture of pure oxygen and nitrogen gases in the proportion of one volume of oxygen to two volumes of nitrogen, and the yield was 590 grams of acid. To study the effects of temperature upon the rate of oxidation, the air supplied to the combustion chamber was raised in temperature by passing it through a porcelain tube packed with asbestos, around which a heating coil of platinum wire was wound. On passing a strong current of electricity through this wire in the tube, the entire system was

elevated in temperature to incandescence, and the air after passing
through was immediately treated in the flaming discharge. This
porcelain tube was cemented directly into the stoneware combus-
tion chamber. A marked decrease in the yield of nitric acid was
noted with the same supply of energy. This behavior is entirely
in accord with the behavior of air when treated to form ozone.
Kowalski describes his apparatus and method for producing nitric
acid from the atmosphere, and states that the yield of product is
largely dependent upon the frequency of the alternating current
used for the flaming discharge. At high frequencies the best re-
sults are attained. Kowalski and Moscicki, working with an
alternating current with a frequency between 5000 and 6000 cycles
per second, obtained 43.5 grams of nitric acid per kilowatt hour
with an amperage in the secondary of .2. They have also con-
firmed the work of McDougall and Howles and others, that the
amperage in the secondary of the transformer has a direct bearing
upon the yield, and that for high current strength the yields of acid
are not so great. The present writer has also fully confirmed this
statement. Kowalski and Moscicki also found that the influence
of the length of the flaming discharge is decided. With a current
in the secondary of only .05 ampere and a difference of potential of
50,000 volts, and a frequency of 6000 to 10,000 cycles per second,
they obtained a maximum yield of nitrous vapors for the energy
employed. They have obtained from 52 to 55 grams of nitric acid
per kilowatt hour, which yield could be nearly doubled by adding
about 50 per cent of pure oxygen gas to the air employed in the
combustion chamber. The work of Bradley and Lovejoy for the
production of nitric acid from the atmosphere upon a large scale is
especially noteworthy. They point out that whereas the silent
electrical discharge, and the spark or disruptive discharge can
cause the combination of oxygen and nitrogen gases, they have but
feeble capacity in point of efficiency, which is also the case with the
ordinary arc. To obtain the best results they point out, as a result
of lengthy researches, that it is necessary to employ an arc divided
into numerous thin and flat subdivisions in order to present a large
surface for a small amount of electrical energy. This work is only
in keeping with that of previous experimenters. They point out that
the thinner the arc the greater the efficiency of the process up to

the point where the arc breaks. It is necessary for best effects to greatly subdivide the current by arranging the arc circuits in parallel. In the experimental apparatus of Bradley and Lovejoy, they employ a direct current of .75 ampere at a pressure of 8000 volts, which can be increased to several ampers at 15,000 volts. There are 138 arcs between which this current is divided, each of which is made and broken by a revolving mechanism 50 times per second. Each arc has a current value of only .005 ampere. The arcs are all produced successively, and not at one time, by a special arrangement of the wire electrodes on the revolving drum which carries them. In their recent apparatus there are 6900 arcs formed and extinguished per second, each arc lasting only for the brief period of 1/20,000 of a second. As each little arc tends to increase in volume, due to increased conductivity as soon as it is formed, the tendency to short circuit the others is avoided by placing inductance-coils in series with the arcs. These small inductance-coils are so designed and calculated that during about 1/40,000 of a second they delay or impede the flow of the current, thereby preventing a rapid growth of the arc, and during the succeeding 1/40,000 of a second, while the arc is being drawn out by the revolving-drum carrier, it sends an impulse which increases the current flow and so prolongs the arc. With a difference of potential of 8000, and about 1/200 of an ampere of current, the arcs are drawn out 4 to 6 inches, and the oxygen and nitrogen treated to this discharge. As in the production of ozone, the molecules of nitrogen oxide must be removed from the field before the atoms of oxygen and nitrogen dissociate, and this point is especially remarked upon by these later investigators. The apparatus installed at Niagara Falls by Bradley and Lovejoy is about 5 feet high by 4 feet in diameter, built of iron of cylindrical form. Six rows of inlet wires, well insulated by porcelain sleeves, enter the sides of this chamber. The terminals of the electrodes are of platinum wire, turned downwards to spread out the arc in a thin flat discharge. In the center of the iron cylinder is a shaft vertically arranged, carrying a series of 23 radial arms, corresponding to the 23 rows of points which enter the sides, there being six radial arms in each plane. These radial arms are each tipped with platinum wire, which come within 1/25 of an inch of the platinum wires of the opposite stationary poles. As the two platinum wire points approach

upon the turning of the shaft, a spark jumps a gap of about $\frac{1}{8}$ of an inch to meet the approaching platinum point, and then the arc is drawn out from 4 to 6 inches by the retreating point until it breaks. If it were not for the little inductance-coils in series with these arcs, it is evident that we would have a comparatively heavy arc at the time of formation, increasing as the points come nearer together. Each of these coils is immersed in oil, and is 5 inches in diameter by 12 inches long, and contains several thousand turns of fine insulated wire. The central shaft carrying the moving electrode points, is turned at the rate of 500 revolutions per minute, and takes a little over 1 horse-power. The efficiency of this piece of apparatus is stated to be 1 pound of nitric acid, per 7 electrical horse-power per hour. Carefully dried air is used in this combustion chamber, which is protected by a coating on the inside of asphalt varnish. If moisture was present in the air, nitric acid would be formed within the chamber, and would in time lead to serious corrosions. The oxides of nitrogen are led to a tower down and through which water trickles, for the production of nitric acid, or a solution of sodium hydroxide, for the production of sodium nitrate. It has been suggested that milk of lime be made to flow through one of these towers for the production of calcium nitrate for fertilizing purposes. This is reported to be a cheaper method of getting nitrogen into the soil than by using sodium nitrate, with lime, at $1.50 per ton. The present writer has experimented with both ozone production and nitric-acid production, employing voltages as high as 250,000, and is able to confirm the results of these experimenters from his own note-book. This field is one of great charm to the student of electrochemistry, and a few concise details as to methods of producing nitric acid from the air may prove welcome to him. Although the foregoing work by others in this line will give the student the fundamental principles involved, and the basic information upon which to experiment, a few specific directions may not be out of order. Let us construct ourselves a simple piece of apparatus of our own design for producing nitric acid by electrical means for use in the laboratory or lecture-room. Fig. 77 shows a simple and easily constructed design of chamber for rotating electrodes, and which has proven most satisfactory in the laboratories of The George Washington University, where it

was built and operated. This chamber consists of a casing of pine wood with an outside diameter of 14 inches, and an internal
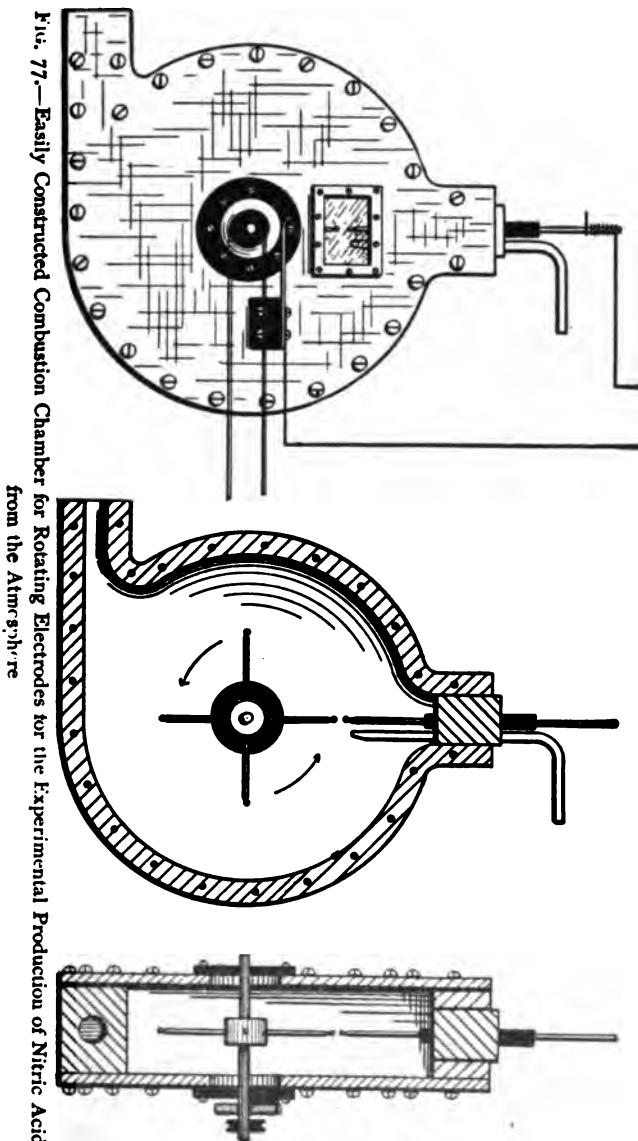
FIG. 77.—Easily Constructed Combustion Chamber for Rotating Electrodes for the Experimental Production of Nitric Acid from the Atmosphere.

diameter of 11½ inches. The internal width of the chamber is 3 inches. The shell for this chamber was cut out on a band-saw at

a lumber mill, and two wooden side plates securely screwed against the sides. The chamber was carefully protected on the inside by several coats of acid-proof paint. The steel spindle which carries the hub into which the four electrodes are screwed, is supported, and turns into holes drilled in two disks of hard rubber, screwed against the sides of the casing. The wood of the casing is cut away at the center so the steel spindle constituting one pole of the high-tension alternating current is in contact with hard rubber only. These circular openings in the wood are 6 inches in diameter, and the diameter of the hard-rubber plates screwed against the sides is 8½ inches. The stationary electrode which protrudes through the top in a vertical position is connected to the other terminal of the high potential transformer, and is carefully insulated from the wooden casing by passing through a hard-rubber tube. There is a brass commutator wheel on the outside, as shown, upon which a brass brush rests, which is in turn supported by a hard-rubber block, as shown. A hard-rubber grooved pulley is on the end of the shaft for the belt of the driving motor. On no account construct this apparatus without the generous use of hard rubber, for in our experimental work it may be desirable to increase the voltage to 16,000 or to even 32,000, and ordinary wooden insulation would be valueless as an effective insulator. An inlet and outlet tube must be provided, as shown, for the air-supply, and a little glass window should be provided to enable us to see the condition of the electrical flame within. Fig. 78 shows this piece of apparatus assembled in connection with a transformer for high potential electrical discharges, a driving motor for the electrodes, a foot-bellows for air-supply, and a Woulf bottle for the absorption of the oxides of nitrogen in either water or caustic soda. The mechanical and electrical conditions set down in one experiment with the present equipment are as follows:

Revolutions per minute of electrodes..........	150
Alternating current cycles per second..........	60
Complete reversals, therefore, per second.	120
Voltage at secondary of transformer..........	10,000
Amperage in flaming arc.	1/25
Jump gap when electrodes were opposite each other in fraction of an inch.	1/16
Length of flaming arc at time of breaking by being drawn out, in inches..............	3½
Appearance of flaming arc.	Pale yellow
Type of transformer.	Oil immersion

With these conditions the yield of nitric acid was excellent, taking in the air at the temperature of the laboratory. This apparatus

FIG. 78.—Combustion Chamber in Connection with Transformer, Driving Motor, Air Supply, Etc.
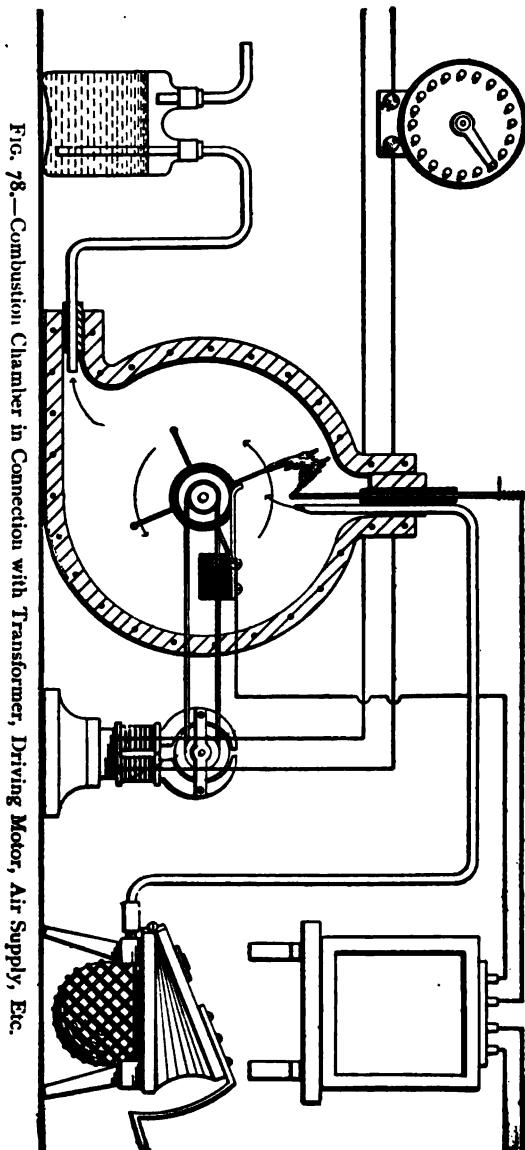
was operated under various conditions and the oxides of nitrogen estimated in several ways. In the place of the Woulf bottle, U

tubes were substituted in several runs, which were immersed in large beakers of liquid air, when the oxides of nitrogen were condensed to a light-blue solid and estimated in this form. It is believed that the construction and operation of this piece of apparatus will fully repay the student having at hand the necessary high potential electrical discharge for the production of nitric acid.

CHAPTER XI.

THE ISOLATION OF THE METALS SODIUM AND POTASSIUM.

By giving specific attention to the metal sodium in this chapter we will also be covering in a general manner the means employed for the isolation of potassium. We will, therefore, refer to sodium in this chapter, and it will be understood that potassium may also be isolated by similar apparatus introduced and used under like conditions. Sodium is much cheaper than potassium, as it is well known by all chemists, because of the greater abundance of cheap sodium salts. As we learned in the opening chapter Sir Humphry Davy was the first to obtain metallic sodium through the agency of the electric current and a mercury cathode. We know that sodium is one of the most abundant of all chemical elements, and that it occurs in immense quantities in combination as rock-salt deposits in saline springs and in sea-water. Sodium also occurs in the form of nitrates, borates, carbonates, etc., etc.

The cheapest source of sodium is, of course, from sodium chloride or common salt. Rock salt forms very considerable deposits in many regions. Among the most important are those at Northwich, in Cheshire, England, where very large quantities are extracted by mining processes.

Sodium has been prepared by an ordinary chemical process by reducing its oxide by carbon at a white heat. The following chemical equation indicates the character of the reaction:

$$Na_2O + C = Na_2 + CO.$$
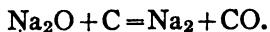
This old process was worked by taking 30 kilograms of dry sodium carbonate, 13 kilograms of charcoal, and 3 kilograms of chalk. These were thoroughly mixed together, calcined, and introduced into iron cylinders heated in reverberatory furnaces. At

a bright red heat the sodium distills over and is collected in suitable receivers. It is purified by redistillation, and then melted under petroleum into ingots which are preserved under naphtha or other suitable hydrocarbon.

Another chemical process devised by Castner, consisted in reducing sodium hydroxide by heating it to a temperature of 850° C. with an intimate mixture of finely divided iron and carbon prepared by mixing the iron with molten pitch. These old chemical methods have been entirely replaced by electrolytic processes, and it is the purpose of this chapter to outline the principle upon which the electrochemical method is dependent. As we have learned, the electrolytic decomposition of sodium and potassium hydroxides led to the discovery of these metals. Sir Humphry Davy, writing in the Philosophical Transaction in 1810, describes his research as follows:

"By means of a stream of oxygen gas from a gasometer applied to the flame of a spirit-lamp, which was thrown on a platina spoon containing potash, this alkali was kept for some minutes in a strong red heat, and in a state of perfect fluidity. The spoon was preserved in communication with the positive of the battery of the power of 100 of 6 inches, highly charged, and the connection from the negative side was made by a platina wire."

This method of Sir Humphry Davy, although theoretically attractive, does not work very smoothly in practice and we will see that very special precautions must be taken in order to get a satisfactory yield of either metallic sodium or potassium. Many modifications of this classic experiment have been made, among which may be mentioned the use of a platinum dish containing a strong solution of potassium hydroxide and metallic mercury in the bottom, which is connected to the negative electrode of a suitable battery. We have here the dawn of the practical processes which followed where the containing vessel is made the cathode in electrolysis. One of the earliest designs of commercial apparatus is that of Charles Watt, which is described in his specifications in 1851. The following account is from his own specifications: "The second part of my invention consists of a mode of preparing or obtaining the metals of the alkalies and alkaline earths by the united action of electricity and heat. For performing this part of my invention by the united action of electricity and heat, I employ a vessel [of the form shown

in Fig. 79], which is made of iron or other suitable material capable of bearing a full red heat. In this figure A is the vessel, which should be at least one-half an inch thick, and, if made of iron, previously to its being used should be coated over its exterior with clay or other substance to preserve it from the action of the fire; B, movable head for the collection of the metals; C, electrodes, with
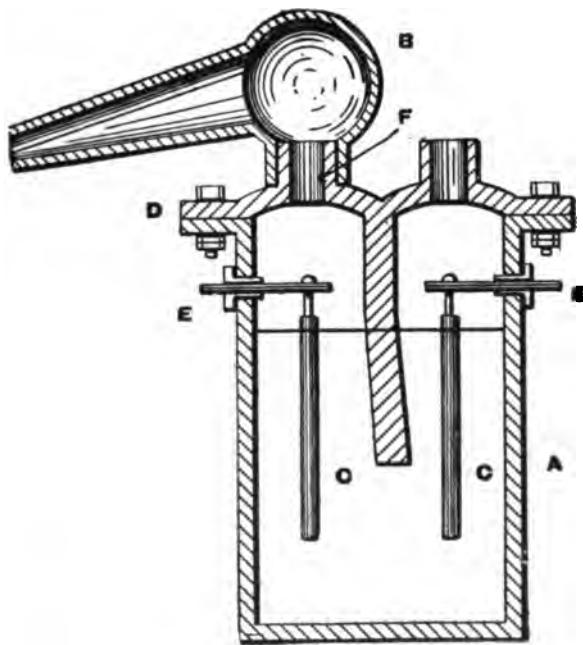
FIG. 79.—Watt's Electrolytic Cell for the Production of Sodium and Potassium.

their attachments E; D, flanges to support the vessel upon the furnace. The covered compartment F, being that in which it is intended to eliminate the metals, is supplied with a carbon electrode and the uncovered compartment is supplied with a gold electrode; but I wish it to be understood that I do not restrict myself to the particular form of apparatus, or to the material to be used for electrodes. The vessel is filled with dry saline matter, so that when it is in a state of fusion it shall reach the dotted lines [the author has shown a full black line drawn across the interior of the cell]; the partition keeps the eliminated substances from reacting on each other, and also

excludes air from the compartment in which the metal is eliminated, the access of which would cause the metal to be oxidized. The vessel is placed in a furnace where it can be subjected to the action of a full red heat, and when the saline matter is in a state of fusion contact is made between the decomposing vessel and the apparatus supplying the electric current or currents, the intensity of which should, at least, be equal to that which would be supplied by 10 cells of Daniell's battery arranged for intensity, but, of course, this depends upon the nature of the salt which is being decomposed. The fused salt is maintained at that temperature which will ensure the instantaneous volatilization of the metal as it is eliminated, and a proper receiver (such a one as is usually employed for the preparation of such metals will answer) is connected air-tight with the narrow tube projecting from the head. The metal is received and preserved in any convenient fluid hydrocarbon. The salts which I usually employ are the chlorides, iodides, or bromides of the metals of the alkalies or alkaline earths."

This historic piece of apparatus proved to be absolutely worthless in commercial practice, for it is impossible to successfully distill such metals in a retort chamber of this peculiar design. There are many weak features about this apparatus which condemn it for all serious uses. The gold anode, apart from its prohibitive cost, would have but a short existence in a fused electrolyte such as he describes where it would be subject to the action in addition of nascent chlorine gas. Numerous forms of sodium and potassium cells had their rise and fall, the majority of them being designed without a suitable knowledge of the severe conditions and requirements for the successful preparation of these metals. One of the early workable designs for a practical sodium cell was that of Borcher, which is illustrated in Fig. 80. The melting-vessel *A* had an opening surrounded by the socket tube *B*, and two other openings with tubular necks *C*. The double socket, which consists of a porcelain tube *E*, fits into the socket as shown, and this receives and supports the upper chamber with its electrode and side tube. This electrode is an iron rod, which is made the cathode of the cell, and is immersed to a proper depth in the fused electrolyte. The anode *F* is of carbon, and is supported in a porcelain chamber provided with a side tube, as shown at *G*. The sodium separates upon the lower part of the cathode and floats

upward, where it is allowed to overflow through the side tube and is collected in a suitable vessel containing a hydrocarbon. An equivalent of chlorine is set free at the anode and escapes by the side tube *G*, where it is either allowed to escape into the atmosphere or be utilized for the production of a by-product. This particular piece of apparatus was designed to take a current varying between 30 and 50 amperes, and returns a yield of about 65 per cent of the weight of
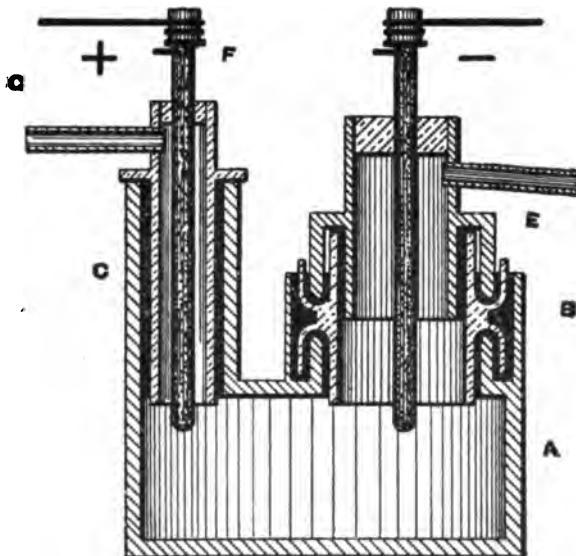
Fig. 80.—Borcher's Design of Cell for the Production of Sodium and Potassium.

sodium theoretically obtainable. The principal objection to be urged against this apparatus of Borcher is its lack of durability and costliness of its parts. It is well known that cast iron has but a limited existence when subjected to the action of alkaline chlorides at a red heat. The porcelain tube *B*, which insulates the cathode compartment from the electrolytic cell is rather intricate in its design. Although it would be out of place here to give such a minute and detailed account of the evolution of the sodium cell as will be found in special works treating the subject of electrometallurgy from the commercial point of view, a brief rev ew of the governing requirements will be given. In many of these pieces of apparatus, metallic sodium

at high temperature and porcelain are brought into direct contact, and there must necessarily be a loss of sodium resulting from the action of the hot metal upon the aluminum silicates of the porcelain. According to Borcher, the following conditions must be observed in the successful design of the electrolytic cells for sodium:

1. "A refractory metal only may be used as a material for a cathode, preferably the better sorts of iron.

2. "The alkaline metal must be collected in, and conveyed from, the cathode cell without coming into contact with any reducible substance.

3. "The walls of the cathode chamber may be made to serve also as cathodes, but in that case they must not be in contact with the electrolyte on the outer surfaces.

4. "The anode must be made of carbon.

5. "The anode compartment must allow of an easy escape for the halogen, and its walls must be made of some material that will withstand the action of the halogens and haloid salts.

6. "The walls of the anode compartment must not be in contact with the separated metal.

7. "No metallic object must be immersed in the electrolyte in any position between the poles or in the path of the current.

8. "The whole apparatus must be of a fire-resisting material."

Without dwelling upon the very numerous forms and patterns of sodium and potassium cells, which have met with more or less success, we will describe the sodium cell as designed and operated by Castner, which fulfills the conditions as tabulated above and has proved itself to be commercially successful. Let us look into the design of a workable Castner cell on a small scale, and describe its mode of operation.

By referring to Fig. 81, the student may become familiar with the design of this cell, which is here illustrated in elevation and section. This particular experimental cell consists of a large inverted iron bottle with a rather large elongated neck. An insulating stopper carrying an iron cathode is passed up through the neck of the bottle, which rests upon a suitable support in order that the bottle portion may be heated by a ring-burner. A metal water-jacket is slipped over the lower part of this neck in order that the insulating stopper and lower portion of the neck may be kept cold. Caustic soda or

potash, as the requirements may dictate, is put into the iron bottle in a molten condition. That portion of the fluid electrolyte which runs down into the lower extremity of the neck, kept cold by the water-jacket, solidifies and forms a seal for the fluid portion of the electrolyte which is kept at the necessary high temperature by the
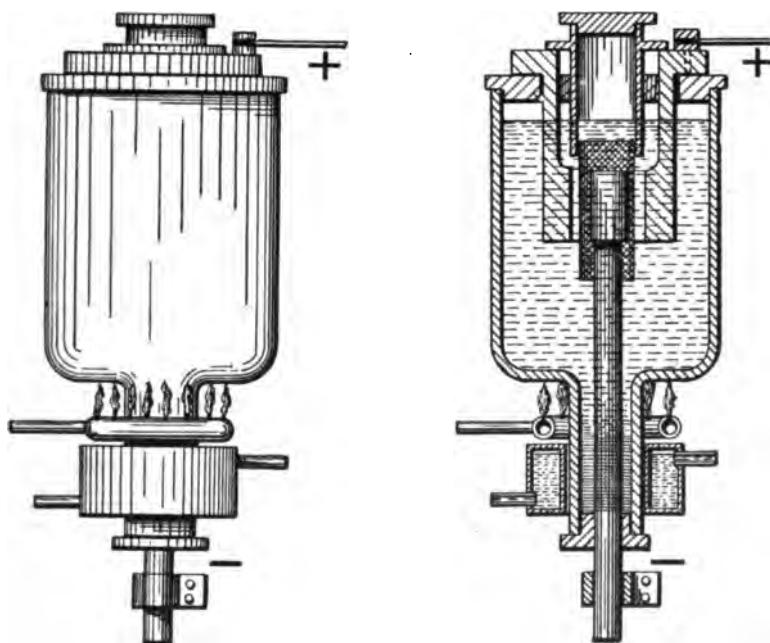
FIG. 81.—Elevation and Section Through Castner's Cell. Experimental Design.

ring-burner. The anodes which, with the present electrolyte, may also be of iron, are suspended from the cover, or they may be cast in one piece of hollow cylindrical form as illustrated in the engraving. Immediately over the end of the cathode is suspended a little cylindrical chamber or receiver for the isolated sodium or potassium. At the lower extremity of this chamber we have a cylindrical wire-gauze guard which, because of the high surface tension of melted sodium, prevents this metal from flowing through, and thereby wandering away from the mouth of the inverted receiver.

For the removal of the fluid metallic sodium, Castner uses a perforated ladle, which retains the metal because of its high solution

tension, while the caustic soda drains away through the perforations. The various parts of the apparatus are insulated by asbestos. With this apparatus hydrogen gas is evolved at the cathode with the sodium, accompanied by the expenditure of a certain amount of electrical energy. We have escaping oxygen gas from the anode compartment. Very large quantities of metallic sodium are produced upon this principle. Fig. 82 shows the various parts of such a Castner cell in
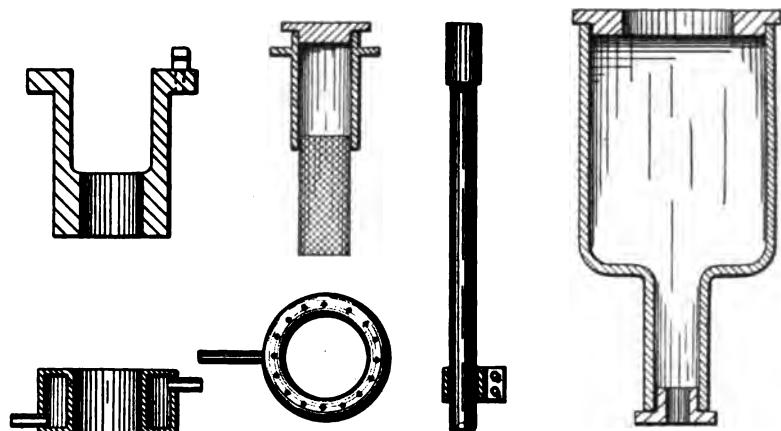
FIG. 82.—Essential Parts of an Experimental Cell of Castner's Type.

detail, and it will be seen that they may be easily made and put together by the student in the laboratory. As will be seen there are only about six or seven important pieces which enter into the construction of this laboratory or experimental cell.

In order to operate this furnace we should have, at least, 50 amperes available and a pressure of about 6 volts. As will be seen from the following simple calculation, an electromotive force of 4.4 volts is just sufficient to drive a current through a fused sodium-hydroxide electrolyte. The heat of combination of NaOH is 102 Calories. The minimum pressure necessary therefor is obtained by dividing the number of Joules represented by 102 Calories, by the constant 96,540. We will remember that the Joule is equivalent to 0.00024 Calorie. 102 divided by .00024 gives us the figure 425,000, from which we obtain the following: $\dfrac{425000}{96540} = 4.4$ volts.

It is a matter of interest to note that hundreds of horse-powers are regularly expended in such sodium cells for the supply of the market of the world. In our next chapter another process, using a fused electrolyte and of still greater commercial importance, will be taken up. This will pertain to the electrolytic manufacture of aluminum.

CHAPTER XII.

THE ISOLATION OF THE METAL ALUMINUM.

ALUMINUM is distinguished among metals as silicon is among non-metals for its immense abundance in the solid mineral portions of the earth, to which indeed it is almost entirely confined, for it is present in vegetables and animals in so small a quantity that it can be scarcely regarded as forming one of their necessary components. Aluminum, as we know, is an extremely important element, both in nature and in the arts. It occurs very widely distributed and very abundantly in many different forms of combination; among them are feldspar, mica, cryolite, and bauxite.

Feldspar is a silicate of aluminum and potassium, of the formula $AlKSI_3O_8$. Mica is a general name applied to a large number of minerals which are silicates of aluminum and some other metal, as potassium, lithium, magnesium, etc. The simplest form of mica is that represented by the general formula $KAlSiO_4$, according to which the mineral is a salt of orthosilicic acid, $Si(OH)_4$. Cryolite is a double fluoride of aluminum and sodium, or the sodium salt of fluoaluminic acid, Na_3AlF_6. Bauxite is a hydroxide of aluminum in combination with a hydroxide of iron. Besides, in the above forms, aluminum occurs in the products of decomposition of minerals. One of the most important of these is clay, which is found in all conditions of purity from the white kaolin to ordinary dark-colored clay. Kaolin is the aluminum salt of orthosilicic acid of the formula $Al_4(SIO_4)_3 + 4H_2O$. Aluminum silicate is found in all soils, but is not taken up by plants, and does not find entrance into the animal body. The name aluminum has its origin in the fact that the salt alum was known at an early date, and the metal was afterwards ioslated from it.

All the compounds of aluminum may be derived from the oxide

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Al_2O_3 and the hydroxide $Al_2(OH)_6$. From the oxide the sulphide Al_2S_3 and the salts which contain alumina as the base are derived, and from the hydroxide the aluminates which are salts containing the aluminum in the acid radical. The preparation of aluminum on a large scale has involved a problem of the highest importance to modern technology. A rough outline of the chemical means for isolating this important metal may not be out of place. As early as 1842 Oërsted attempted the decomposition of aluminum chloride through the agency of a potassium amalgam, but the success of his work is open to considerable doubt, for subsequent workers endeavoring to follow his directions were unsuccessful in obtaining any metallic aluminum. Three years later, however, Wöhler successfully reduced the chloride by using potassium. Deville working at a later date produced this important metal through aluminum chloride, by resorting to the use of the double chloride of aluminum and sodium. Instead of the costly potassium, the far cheaper metal, sodium, was used. For twenty-five or thirty years this process was carried on in France, and for a time it was also used in England. Rose in 1853 proposed the substitution of cryolite for the chloride and used magnesium in the place of sodium. Grabau's process, which is of much later date, is of special interest, for it is of unusual merit, as may be seen from the following equation, where solutions of sulphate of alumina are first treated with cryolite to obtain aluminum entirely as fluoride $Al_2(SO_4) + Al_2F_6 = 2Al_2F_6 + 3Na_2SO_4$. The aluminum fluoride being insoluble in water, is filtered off, washed and dried, and heated to a low red heat, when it is at once charged into a cold vessel lined with pure cryolite. The required quantity of metallic sodium is now placed in upon the hot material and the vessel covered. Accompanied by a great liberation of heat energy the reaction takes place, which may be represented by the following equation: $2Al_2F_6 + 3Na_2 = Al_2 + Al_2F_6.6NaF$. The aluminum, after the reaction has taken place, is recovered melted into a metallic mass at the bottom of the chamber, but covered over with a slag of cryolite, which itself has been completely fused through the high temperature of the reaction. This is a workable scheme for the production of aluminum, but it is evident at once that the economy of such a process depends upon the cost of sodium.

The electrical production of metallic aluminum may be divided

into two different schemes, one where the metal is obtained by the reduction of its oxide and the other by a typical case of electrolysis. Let us first look into the processes of reduction. For a long time alumina, which is the oxide of aluminum, was held to be unreducible. In the electric furnace, however, with sufficient current density, the oxide may be reduced in the presence of carbon. This electro-reduction is non-electrolytic, being simply brought about by the
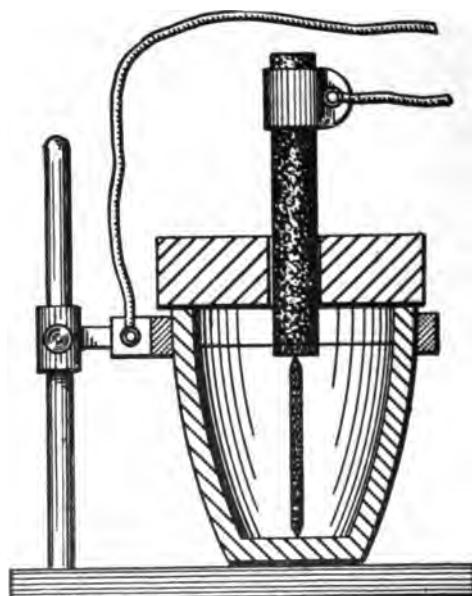
FIG. 83.—Laboratory Furnace for the Reduction of Alumina. Experimental Design.

intense heat of the electric furnace. With a sufficient current density, it appears to-day that no oxide can withstand the high temperature of the electric furnace. Let us impress upon a small quantity of alumina this powerful reducing action of carbon at the temperatures accompanying a high current density electric arc. Fig. 83 shows a handy laboratory furnace for accomplishing this. We have firmly clamped in an iron ring a graphite crucible which also rests upon the iron base of the ring-stand. A large carbon rod fed through an opening in a fire-clay cover serves as the other electrode. The charge of alumina and pulverized carbon is placed in the crucible

around a slender conducting pencil of carbon to start the electric current. A very heavy current is essential to bring about the reduction. According to Borcher, a current density of about 3500 amperes per square inch will bring about this reduction. A current of 6500 amperes per square inch is sufficient to reduce any metallic oxide known. The electromotive force need not be high, 15 volts being ample for a small furnace. About 53 electrical horse-power are therefore necessary. Fig. 84 shows a horizontal furnace for the
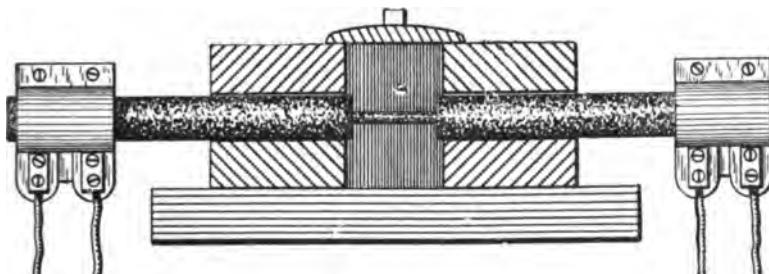
FIG. 84.—Furnace for the Reduction of Alumina.   Practical Design.

reduction of alumina on a somewhat larger scale. In our small crucible furnace, the carbon pencil can be, of course, less than an inch in sectional area, permitting the use of a smaller amount of current. With one-tenth of an inch in sectional area for our carbon pencil, we can reduce a small quantity of alumina with one-tenth the current strength. These furnaces are known as resistor furnaces and are easily constructed and operated. Carbon pencils of $\frac{1}{8}$ inch sectional area effect a very complete reduction with a current of 40 amperes. Let us look into the electrolytic methods of isolating aluminum, and to this end we will first refer to Deville's apparatus. The following is a translation from Deville's original paper: "Up to the present time it has appeared to me impossible to obtain aluminum from aqueous solution by means of a galvanic battery; and I should even now believe in the absolute impossibility of doing so if the brilliant experiments of Bunsen in the production of barium, chromium, and manganese had not shaken my convictions. However, I am compelled to say that all the processes of this kind which have been published recently in reference to the preparation of

aluminum have given me only negative results.   Every one knows
the beautiful process by means of which Bunsen has produced
magnesium by decomposing magnesium chloride with the aid of a
galvanic battery. The illustrious Professor at Heidelberg has
opened a way which may lead to results that will be interesting from
many points of view. However, there can be no hope of applying
the battery to the direct decomposition of aluminum chloride,
which is a substance which does not fuse, but that volatilizes at a
low temperature; it is nececsary, therefore, to find a composition
for the metallic bath that shall involve the use of a fusible material,
from which aluminum alone can be deposited by the electric current.
I have found such a substance in the double chloride of aluminum
and sodium, the production of which is a necessary feature of the
extraction of aluminum by sodium.   This chloride, which is fusible
at about 185° C., and remains fixed at a sufficiently high tempera-
ture, although it is volatile at a temperature above the fusing point
of aluminum, fulfills all the required conditions. I introduced this
substance into a porcelain crucible, which was imperfectly separated
into two compartments by a plate of biscuit porcelain, decomposed
it by means of a battery of five elements, using carbon electrodes,
the crucible being heated and the temperature being increased con-
tinually in order that the charge might be maintained in a fluid con-
dition as it became gradually less and less fusible; but the fusing
temperature of aluminum was not exceeded.   Arrived at this point,
I stopped the experiment, and, after lifting out the diaphragm and
the electrodes, I heated the apparatus to a bright red heat, and found
at the bottom of the crucible a regulus of aluminum, which was
rolled and was exhibited to the Academy at its meeting on March
20th, 1854. It was accompanied by a considerable quantity of
carbon, which had prevented a notable portion of the metal from
uniting into a single mass. This carbon resulted from the disinte-
gration of the very dense sample of retort carbon that served as
electrode; and as a result of this action the positive electrode was
entirely eaten away in spite of its thickness, which was very con-
siderable. This disposition of apparatus (as used by Bunsen for
magnesium) was not convenient in the case of aluminum; and the
process to which I have been led, after many experiments, is as
follows: The aluminum bath is prepared by weighing 2 parts of

aluminum chloride and adding to it 1 part of marine salt in the state of dry powder. The whole is mixed in a porcelain crucible heated to about 200° C. Combination shortly sets in with evolution of heat, and there results a very fluid mixture, which is a bath used for the decomposition.

"The apparatus [as shown in Fig. 85] consists of a glazed porcelain crucible A, which, as a measure of precaution, is placed within the somewhat larger fire-clay crucible B; the whole is surmounted by a
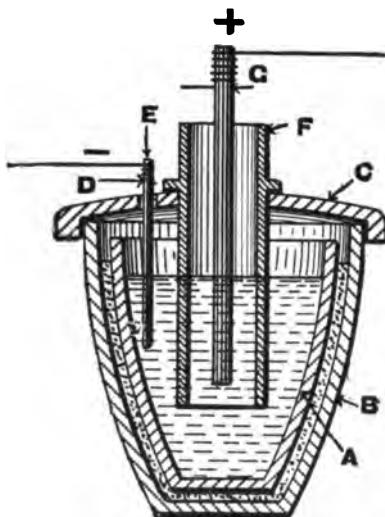
FIG. 85.—Deville's Cell for Experimental Work.

crucible cover C pierced with a slot D, through which is placed a wide and stout sheet of platinum E to serve as negative electrode, and with an aperture in which is tightly fixed a well-dried porous cell F. Within the latter is placed a rod of retort carbon G as positive electrode. The bottom of the porous cell should be kept at the distance of some centimeters from that of the porcelain crucible. The porcelain crucible and the porous cell are filled to the same level with the fused aluminum-sodium chloride, and the apparatus is heated after the manner described. The electrodes are then introduced and the current is passed through the apparatus. Aluminum is deposited with some sodium chloride upon the platinum plate, and chlorine together with some aluminum chloride is disengaged

in the porous cell; fumes are thus produced which are destroyed by introducing dry and powdered marine salt at intervals into the porous cell. This salt is transported to the negative pole during the operation along with the aluminum. A small number of elements (two are actually sufficient) are required to decompose the chloride, which presents only a feeble resistance to the electric current.

"The platinum plate is raised from time to time as it becomes sufficiently charged with metallic and saline deposit. It is allowed to cool, the mass of salt is rapidly broken, and the plate is replaced in the circuit. The crude material detached from the electrode is fused in a porcelain crucible enclosed within a fire-clay crucible. After cooling, the mass is treated with water, which dissolves a large quantity of sodium chloride; and a gray metallic powder is left, which is reunited into a regulus by several successive fusions. Addition of double chloride of aluminum and sodium is necessary during each fusion."

This process of Deville may be said to have marked the dawn of the successful processes dependent upon the electrolysis of fused aluminum compounds. As it would require a great deal more space than we are able to give to the subject in a general work, to enumerate and describe the various steps in the evolution of aluminum reduction cells, we must content ourselves with an outline of the more important processes. Let us look into the method of Hall, and for this purpose we may best turn to the specifications and drawings of one of his patents. The following is from the patent of Hall of 1886, and reads as follows: "The invention described herein relates to the reduction of aluminum from its oxide by dissolving such oxide in a bath containing a fused fluoride salt of aluminum, and then reducing the aluminum by passing an electric current through the bath, substantially as hereinafter more fully described and claimed. In the accompanying drawings, [Fig. 86] represents a sectional elevation of a form of apparatus applicable in the practice of my invention, and [Fig. 87] is a view partly in elevation and partly in section of a modified form of apparatus.

" In the practice of my invention I prepare a bath for the solution of the aluminum by fusing together in a suitable crucible, *A*, the fluoride of aluminum and the fluoride of a metal more electropositive than aluminum, as, for example, the fluoride of sodium,

potassium, etc., these salts being preferably mingled together in the proportions of 84 parts of sodium fluoride and 169 parts fluoride, represented by the formula Na_2F_8. A convenient method of forming the bath consists in adding to the mineral cryolite $\frac{338}{421}$ of its weight of aluminum fluoride. The object of thus adding alu-
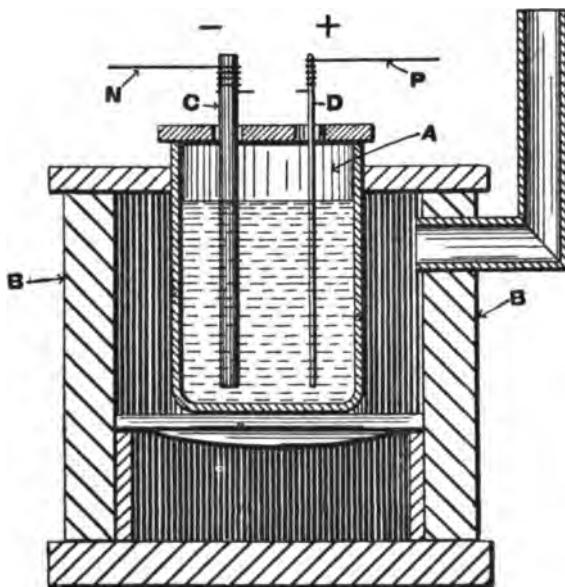
FIG. 86.—Hall's Electrolytic Cell and Furnace for the Production of Aluminum.

minum fluoride is to secure in the bath the proper relative proportions of the fluorides of aluminum and sodium. To the fused bath is added alumina, or the oxide of aluminum, in sufficient quantities, and the alumina being dissolved by the fused bath an electric current is passed through the solution by means of suitable electrodes, C and D, connected with a dynamo-electric machine or other suitable source of electricity, and immersed in the solution. By the action of the electric current, which preferably has an electromotive force of about 4 to 6 volts, oxygen is released at the positive electrode, C, and aluminum is released at the negative electrode, D, which, on account of the affinity of aluminum for other metals, is formed of

carbon when it is desired to produce pure aluminum.   The positive
electrode may be formed of carbon, copper, platinum, or other
suitable material.   When formed of carbon the electrode, C, is
gradually consumed, and must therefore be renewed from time to
time; but when formed of copper an oxide coating is formed over
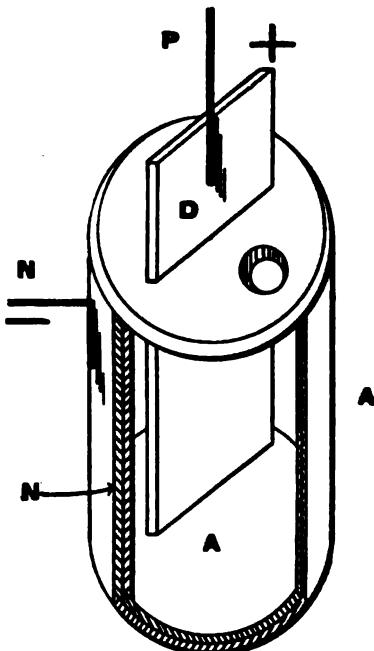
FIG. 87.—Experimental Cell of Hall.

the surface of the electrode.   This coating serves to protect the
electrode from further destruction by the action of the oxygen, but
does not interfere materially with the conducting qualities of the
electrode.

"On account of the affinity of the aluminum for other metals,
and also the corrosive action of the materials, I prefer to form the
crucible, or melting-pot A, of metal—as iron or steel—and protect
the same from the action of the aluminum by a carbon lining, A.
This crucible is placed in a suitable furnace, B, and subjected to a
sufficient heat to fuse the materials placed therein, such materials
fusing at approximately the same temperature as common salt.

"In lieu of the electrode D [Fig. 86], the carbon lining, A, may be employed as the negative electrode, as shown in [Fig. 87], the conductor from the negative pole of the electric generator being suitably connected, as shown at N, to such lining.

"In order to render the bath or solvent more fusible, fluoride of lithium may be substituted for a portion of the fluoride of sodium; as, for example, for one-fourth the fluoride of sodium an equivalent amount of lithium fluoride by molecular weights may be substituted. Thus 26 parts of lithium fluoride displacing 42 parts of sodium fluoride, the resulting combination contains 26 parts of lithium fluoride for every 126 parts of sodium fluoride, and 338 parts of aluminum fluoride.

"While I consider the proportions of fluorides of sodium and aluminum, and of the fluorides of sodium, lithium, and aluminum hereinbefore stated, are best adapted for the purpose, such proportions may be varied within certain limits without materially affecting the operation or function of the bath, as in fact, any proportions which may be found suitable may be employed. The aluminum, as it is reduced at the negative electrode, is melted and collects thereon in globules, and then drops down to the bottom of the bath, which is of lower specific gravity than the molten aluminum, and can be removed by suitable means; or the bath may be poured out, and after being cooled the aluminum can be picked out."

Fig. 88 shows the scheme finally adopted by Hall for the production of aluminum by the electrolysis of fused salts. According to this later patent the following bath is employed: "Fluoride of calcium, 234 parts; cryolite, the double fluoride ($Na_6Al_2F_{12}$), 421 parts; the fluoride of aluminum, 845 parts, by weight, and about 3 to 4 per cent of a suitable chloride, e.g., calcium chloride. Alumina is then added to this bath, preferably in sufficient quantities to form a saturated solution. Electrodes are then inserted in the bath, the negative electrode being formed of carbon when pure aluminum is desired. The positive electrode may be formed of carbon or other suitable material. This piece of apparatus, as the drawing indicates, consists of an iron trough lined with plates of carbon. A heavy copper connector is riveted to the outside of this trough and connects with the negative lead of the dynamo. The iron trough, therefore, with its carbon lining serves as a cathode. The anodes consist

of carbon rods suspended from a heavy copper bar in such a way that they may be lowered into the electrolyte. As these carbons are slowly consumed by the oxygen liberated in contact with them, it is necessary to have such an adjustment for feeding them into the bath. It is interesting to note that with such a system the weight of carbon burned by the nascent oxygen is about equal to the metallic aluminum produced. The carbon lining is but very slowly altered and lasts for a long time. The electrolysis consists in the decomposition of alumina dissolved in the fused bath. Several such troughs in practice are connected up in series for the commercial production of this important metal. In this plan of operation the
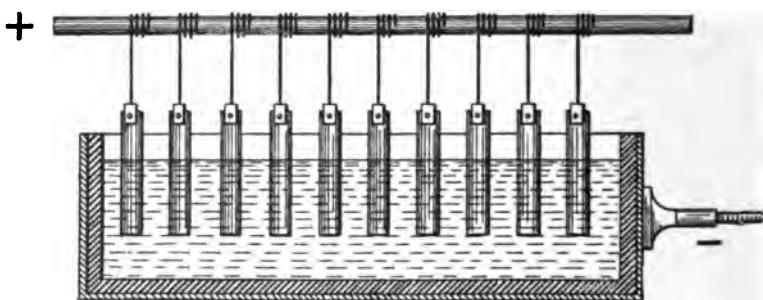
FIG. 88.—Hall's Approved Aluminum Cell.

heat required to keep the electrolyte fluid is derived from the electrolyzing current. Immense quantities of aluminum are produced upon this general principle. The next device which we will consider is that of Héroult, as depicted in Fig. 89. This process may produce either metallic aluminum or aluminum bronze, the latter being an alloy of aluminum and copper. In this piece of apparatus the electrolyte consists of alumina dissolved in fused cryolite, or in an artificial mixture of aluminum fluoride with sodium fluoride. The electrolyte is maintained in the molten state by the heat generated by the passage of the electrolyzing current. In the illustration we have a heavy iron vessel lined with carbon plates, with tap-hole for allowing the molten alloy to be drawn off. A heavy carbon cover with a suitable opening for the anodes is put in place to prevent undue loss of heat from radiation. The anodes are connected as shown to a common holder-bar, and are of carbon hung in such a

way that they may be lowered into the electrolyte as they are consumed. The operation of the process is started by placing some pure copper in the bottom of the furnace and lowering the anodes until they come in contact with the metal. The intense heat of an arc so established fuses the copper, when the electrolyte is added, which, of course, rapidly assumes a fluid state. Cryolite is added until a sufficient depth has been attained and the electrolysis of the
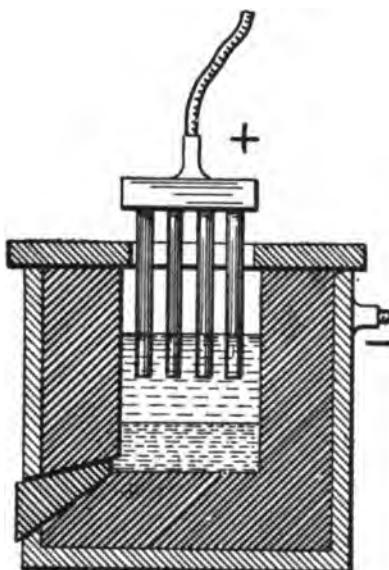
FIG. 89.—Héroult's Aluminum Cell.

alumina which is dissolved therein takes place between the molten copper as cathode and the immersed carbon rods as anodes. Aluminum separates at the molten copper and alloys with it, the product being allowed to run off at intervals. Additional quantities of copper and alumina are fed in in the proper proportions from time to time to form a suitable alloy. It may be seen that the furnace and its operation are equally well adapted for the production of pure aluminum, if some of this metal is placed in the bottom of the furnace instead of copper, when the process is first started, which then approaches very closely the device of Hall.

CHAPTER XIII.

THE ISOLATION OF CALCIUM.

CALCIUM is more generally met with in a state of chemical combination than any other metal, for it occurs in enormous quantities in limestones and chalks, and in the minerals gypsum, fluorspar, apatite, etc., etc. Yet, notwithstanding its great abundance in combination, because of the great difficulties in isolating it, the metal is exceedingly scarce and seldom met with in the laboratory. Let us look a little into the properties of this interesting metal, and the chemical methods of preparing it, before undertaking to obtain it by electrolysis, which is by no means an easy task. Calcium is usually described in the text-books as a brass-yellow metal of lustrous appearance, which in moist air soon becomes covered with a coating of calcium hydroxide and calcium carbonate. Calcium decomposes water just as potassium and sodium do, but the heat of the reaction is not sufficient to set fire to the hydrogen which it evolves. Calcium, because of the expense and difficulty in obtaining it, has never had any useful application except in the most special cases on very small scales in some research work. Before the electrolytic method of isolating calcium, it was obtained at a great cost by purely chemical means. The following method will be of interest to the student in general chemistry and will serve as an introduction to the electrical means. For example, calcium may be obtained as a finely divided substance by heating powdered lime with powdered metallic magnesium, as shown by the following simple equation:

$$CaO + Mg = MgO + Ca.$$
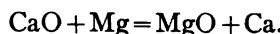
After the reaction has taken place, the presence of calcium may be shown by adding a little distilled water to the mass in a tube, when the free calcium reacting with the water will set hydrogen free, and

in addition, the presence of lime-water in the tube may be shown. Another chemical method consists in making a zinc calcium and distilling off the zinc by heating to a high temperature in a gas-retort carbon crucible. The zinc calcium is made by melting together a mixture of calcium chloride, zinc, and metallic sodium. The sodium decomposes the chloride, and the reduced calcium dissolves in the zinc as soon as it is liberated. Metallic calcium when heated to redness burns with a very brilliant white light and is converted into its oxide. Modern text-books on general chemistry state that it is obtained to-day by electrolyzing its fused chloride, but they do not, of course, undertake to dwell upon the details of the operation or to even state the great difficulties involved. The electrolytic isolation of metallic calcium is far from easy, and its electrolytic preparation is introduced here to show the student in electrochemistry that his skill and resources will often be taxed, and at times very severely.

As intimated, therefore, while theoretically simple, the extraction of calcium from its chloride by electrolysis is attended by extreme difficulty as compared with certain other metals. It may be stated in general that the three metals of the alkaline earths are exceedingly difficult to isolate. Bunsen and Matthiessen were the first to isolate these metals from their chlorides in their pure condition. Failure after failure attended their efforts to extract these metals in Bunsen's laboratory by electrolyzing their chlorides, using apparatus such as we described in a previous chapter for the production of metallic magnesium from its chloride. In the year of 1854, however, Bunsen, as the result of his carefully conducted research, was able to point out the reason for the failures. The following interesting and note-worthy observation was made by Bunsen, which should be impressed upon the students of electrochemistry, as Bunsen's discovery has great bearing upon many cases in this field. We will quote his own words, which are as follows: "The density of the current used for electrolysis—that is, the ratio of current volume to electrode—area exerts a most important influence on its chemical effects. The power of the current to overcome affinities increases with this density. Of no less importance is the relative mass of the constituents of the electrolyte through which the current passes." To put Bunsen's suggestion into practical operation we must have, therefore, means

for electrolyzing calcium chloride and a suitable container for the same with adjustment for high current density. It has been found in experiment and practice, that exceedingly high current density at the cathode is absolutely essential for the isolation of calcium. In order to secure conditions of exceedingly high cathode current density special designs of apparatus are necessary. High cathode current density involves small cathode area, and a current which gives rise to very high temperature, even beyond the melting-point of iron and steel. It is, therefore, necessary to provide some means for keeping the cathode cold, or comparatively cold. Means must also be provided for preventing, as far as possible, the recombination of the liberated chlorine with the freed calcium. The device as illustrated in Fig. 90 embodies these set requirements upon an experimental scale. Here we have a small calcium reduction-furnace illustrated in both elevation and section. The chamber, for the calcium chloride to be electrolyzed, consists of a large graphite crucible, not less than 5 or 6 inches in diameter, with the bottom sawed off, giving us in reality a large graphite collar. This graphite crucible has clamped to its exterior a heavy iron band and serves as an anode in the operation. This bottomless crucible, or collar, rests upon and may be cemented to a disk of mica, which in turn rests upon a cylindrical water-bath, as shown. This water-bath has a tube soldered within its center, which receives with a tight fit the turned rod or bar of iron not less than an inch in diameter. This rod is long enough to go up through the bottom of the bath and attached mica covering, which forms the bottom of the graphite crucible, extending a couple of inches below and having a stout clamp of iron connected with the lead of the dynamo. The cathode proper consists of a piece of steel wire about 1/16 of an inch in diameter and about 3 inches in length, which is securely screwed into the upper end of the iron bar. When the water-bath is filled with cold water and means provided for a continuous circulation through it from a spigot, the cathode wire may give up its heat by conductance down into the iron bar, which in turn gives up its acquired heat to the circulating water. In this way it is prevented from getting too hot. A cylinder of platinum-wire gauze about 1½ inches in diameter goes over the cathode wire, as shown, to prevent the liberated calcium from wandering about in the electrolyte. To

put such a furnace in operation it is assembled, with the exception of the platinum-gauze cylinder and cover, when the cathode bar is

FIG. 90.—Elevation and Section of an Experimental Furnace for the Isolation of Calcium.
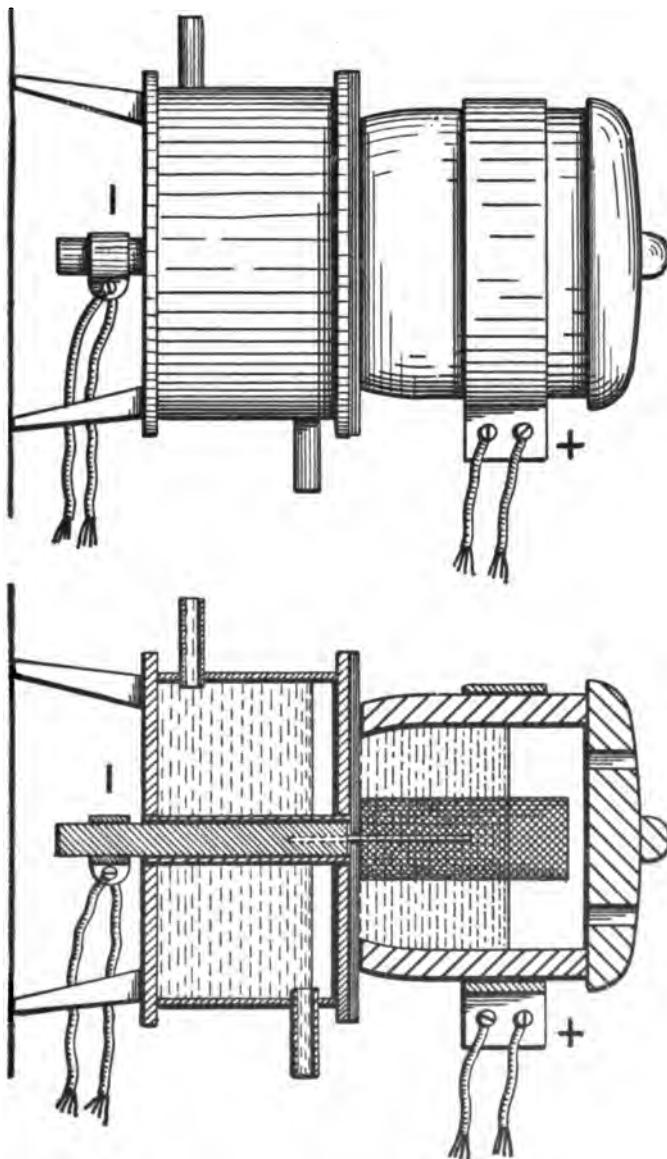
put in proper electrical connection with a suitable dynamo. The dynamo should be capable of giving at least 100 amperes at a pres-

sure of about 60 volts. The calcium chloride in lumps is slowly added, a small quantity at a time, and by means of an iron rod a small arc is established between the cathode wire and the side of the crucible until a small quantity of the calcium chloride has been fused down to a fluid state, which will then conduct the electric current. More chloride is added until the crucible is about three fourths filled. If means are at hand for melting a sufficient quantity of calcium chloride separately, and pouring into the crucible, the process may be more quickly put in operation. When the crucible is filled with fluid electrolyte, the temperature is easily maintained at the melting-point of the substance by the current, and then the platinum-wire cylinder should be put in position. The calcium will separate in little globules from the cathode and be retained within the platinum-gauze cylinder, while the chloride will escape from walls of the crucible, which act as anode, and pass out through the covering. The author is describing a successful run upon this design of furnace. It is very easy to have an unsuccessful run, and if the conditions are not just right the attempt will result in failure. For instance, it is not really possible, so far as the experiments of the present writer go to show, to isolate calcium with less than 60 amperes, with a design and dimensions similar to those given. If, on the other hand, too heavy a current is used, the steel-wire cathode will, in spite of its connection with the mass of iron in the water-bath, rise so rapidly in temperature that it will melt off. On the other hand, if the current is not strong enough to keep the entire mass in fusion, a solid crust of calcium chloride will form on top of the molten chloride and offer a resisting seal to the chlorine gas, which is being given off from the lower portion of the crucible walls. Should such a crust form it should immediately be punctured to allow the chlorine to escape, or it will lift the crucible with almost explosive violence from the mica disk, even if it has been securely cemented down, and a stream of fluid electrolyte will be forced out. With everything working smoothly, the calcium may be ladled out from the interior of the platinum-wire cylinder by means of a small iron spoon perforated to allow the fused electrolyte to run through, the calcium remaining within the ladle, because of its high surface tension. This calcium is liable to take fire in the air and burn with a fierce white light, and a suitable hydrocarbon in a wide-mouth vessel

should be ready in which to immediately plunge the liberated metal. By referring to Fig. 91 the separate essential parts of such a laboratory furnace may be seen, which are, namely: a water-bath, insulating mica disk with a small hole through its center, just the size of the cathode wire, and a platinum-wire-gauze cylinder together with a heavy iron bar with its cathode screwed in, and a bottomless crucible. As the calcium industry is comparatively unimportant,
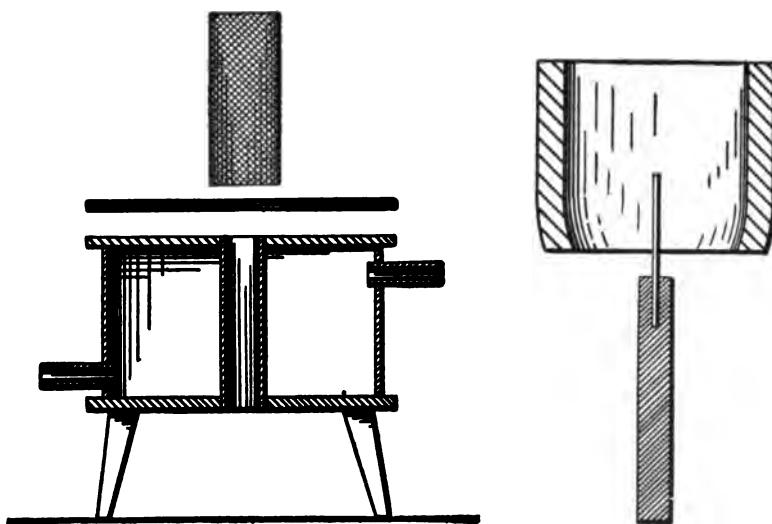
FIG. 91.—Essential Parts of Experimental Furnace for the Isolation of Calcium.

we will content ourselves with only one more design of calcium furnace, and for this purpose we will turn to Fig. 92. This design we owe to Borscher, as given here in elevation and section. The outer casing is in the form of a long thimble and may be of almost any convenient size. This thimble serves as anode, which may be of iron, brass, or nickel. In the bottom of this elongated thimble tube is placed a small porcelain crucible of such a size that it will just slip within the tube. The cathode is a piece of steel wire between 1/16 and 1/8 of an inch in diameter and about 1 inch in length, screwed into a concave end of a similar tube which is supported by an insulating collar as shown. Within the center of this tube, which may be supported by a middle collar brazed or soldered in position, is the cooling water, which falls directly upon the end

of the tube carrying the cathode wire, and discharging from the outlet tube at the right, as shown. With such a device the inner tube is kept cold, giving up the heat generated at the cathode wire which it supports. The insulating collar or support is provided with a small side tube for the escape of chlorine gas. To put the furnace in operation the little porcelain crucible is dropped within the elongated thimble, and the whole tube is filled about two
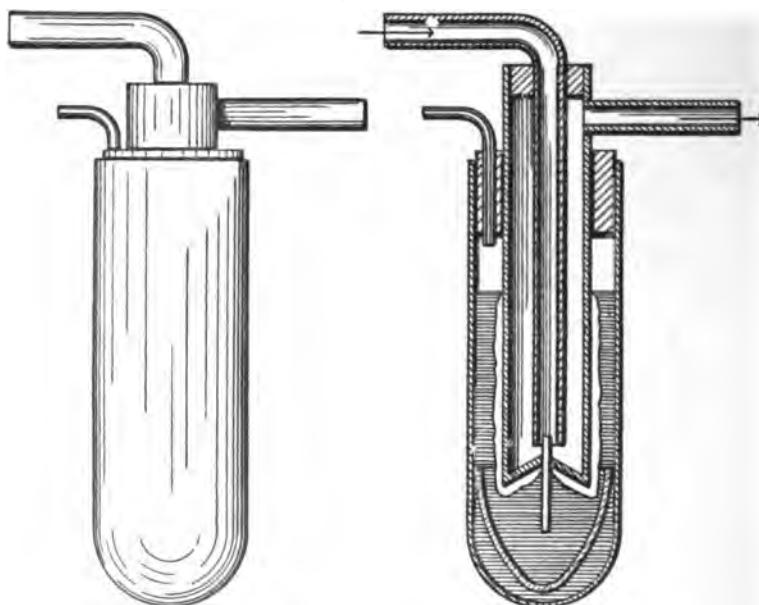
Fig. 92.—Experimental Calcium Furnace. Borscher's Design.

thirds full of calcium chloride fragments, which may be melted down by holding the tube in the flame of a Bunsen burner. When in the fluid state, the electrolyte receives the water-jacket tube and cathode wire, which, being at a low temperature, immediately chills the calcium chloride to the point of solidification. This has been indicated in the drawing by the white mass surrounding the water-chamber. The cell is immediately placed in circuit with the electrical supply, when the Bunsen burner may be removed and the temperature of electrolysis maintained by the passage of the current. Calcium isolates from the steel-wire cathode in small globules, and if it rises it is caught in the concave end of the water-jacket. The little

porcelain crucible serves a double purpose, namely, in catching any metallic calcium which may fall if specific gravity conditions of the electrolyte so induce, but more especially to prevent any chlorine gas from rising and reuniting with the isolated calcium. It will be at once appreciated that no chlorine will be liberated from the interior of this porcelain crucible, for being of a non-conductible material it does not act as an anode. There is, in consequence, no chlorine given off which may reach the cathode at a point lower than the upper edge of this crucible. This device of Borscher is one intended for producing small quantities of calcium and must be directly taken apart in order to secure such fragments of metal isolated. It is, nevertheless, a furnace of neat design, and very useful for experimental work upon a small scale.

CHAPTER XIV.

THE ELECTRIC FURNACE AND FURNACE PRODUCTS.

ELECTRIC furnaces may be roughly classified into two general kinds, those for the attainment of moderate temperatures and those for the attainment of the highest temperatures within the reach of man. By moderate temperature, we may consider furnaces capable of running up to about 1500° or 1600° C: It is this first type of furnace which will now occupy our attention. Both general types of electric furnaces are convertors of electrical energy into heat energy and both types depend upon resistors. The resistors in the type of furnace which we will consider first consist of platinum wire, and because of the facility and ease with which the temperature may be regulated, find a most useful place in all chemical and electrochemical laboratories. Having had considerable success with the furnace here depicted it is deemed of value to describe more or less in detail the method of assembling and constructing such small furnaces of a great range of general utility. Fig. 93 illustrates a side view of a small muffle furnace which may be very easily put in operation and regulated. It consists, as shown, of an iron retort stand with a clamp holding in a horizontal position a fire-clay tube which is wound with platinum wire, having slipped over the platinum wire winding a second somewhat larger fire-clay tube. The terminals of the platinum wire are connected with a lamp-bank, together with a 110-volt or 220-volt electric lighting system. In order to make the construction of this furnace clear, we will turn to Fig. 94. where the smaller tube is shown turned down and spirally threaded to receive the platinum-wire winding. It is over this portion of the fire-clay tube that the outer jacket is placed. There are numerous kinds of fire-clay, which, before baking may be turned on the lathe with facility and alter but little in shape and dimension after the

firing process. In this last figure referred to, an end view of the furnace is given, together with a side elevation of the muffle tube. A good size for such a furnace is to have the inner tube, upon which the platinum wire is wound, about 5 inches long with an internal diameter of about 1½ inches, and an external diameter of about 2 inches. Where the tube has been turned down and the spiral cut
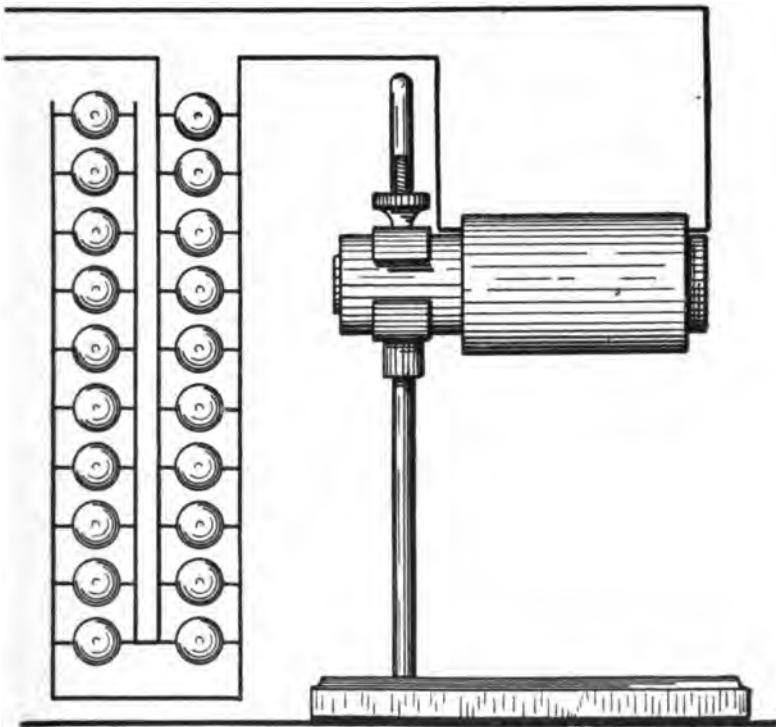
FIG. 9.—Elevation of Muffle Furnace and Lamp-bank.

on, the thickness should not be over 3/16 of an inch. Of course, these dimensions may be varied to meet different requirements, but for studying the behavior of certain bodies at different temperatures only a small quantity of these bodies is necessary for the examination. At least two meters of platinum wire should be wound on a single furnace, the wire to be about number 22 gauge. It will require some preliminary experiment with each furnace in connection with the lamp-bank and suitable ammeter in series to

ascertain how much current the furnace will stand with the out
side muffle in place. It is, of course, an easy matter to burn out
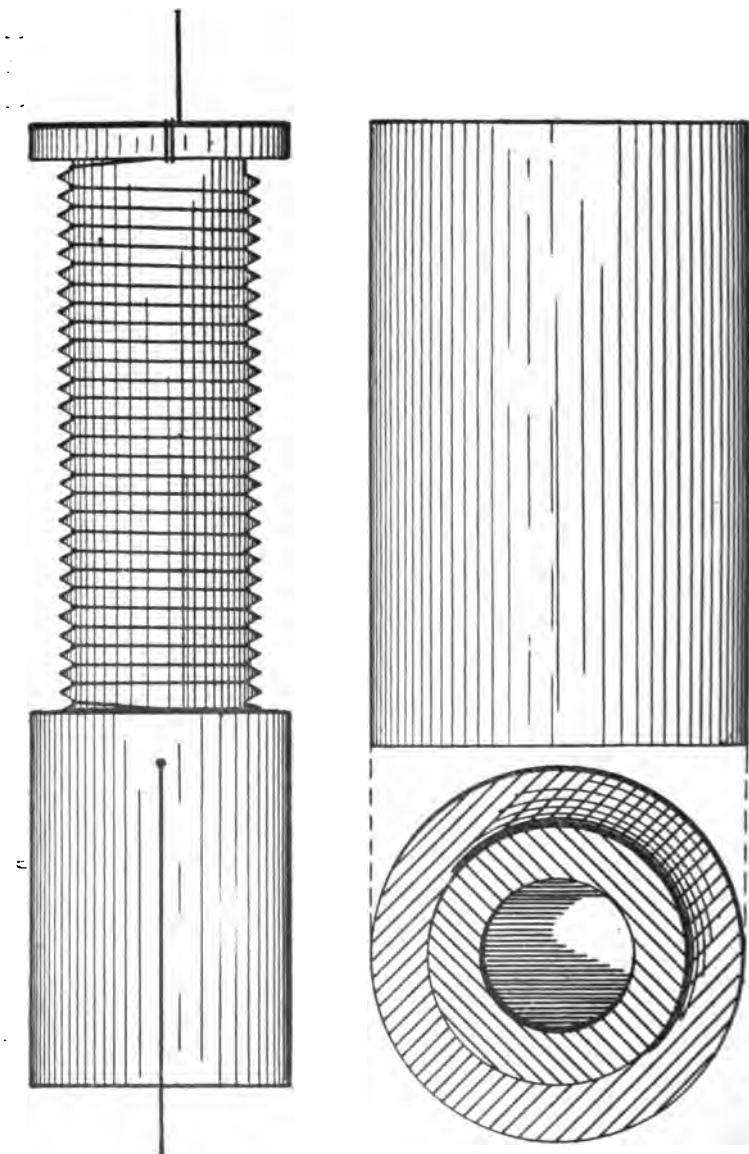
FIG. 94.— Elevation of Furnace with Muffle Removed showing Platinum Wire-winding.

the platinum wire, but such a mishap is not usually very serious,
for the wire is apt to fuse at a certain point, when it may, of course,

be quickly welded together again.   After a mishap of this kind
the experimenter will be in possession of valuable data in connection

FIG. 95.—Section through Muffle Furnace Showing Interior.
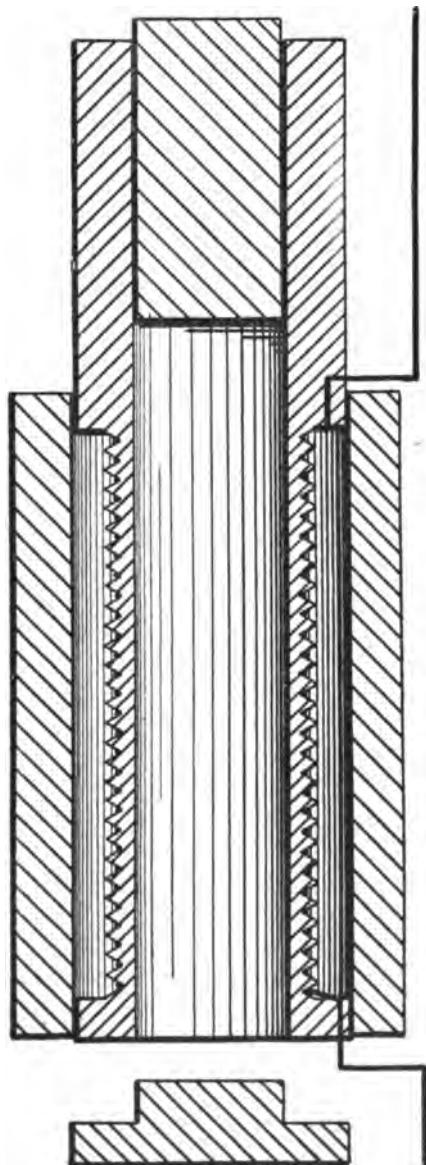
with his furnace if he has slowly admitted the current to it through
a suitable ammeter.   By referring to Fig. 95 a sectional view through

a completely assembled furnace may be seen. The furnace is here indicated with a fire-clay plug in one end and a similar plug of light design at the other end. The furnace may be brought to bright incandescence within a very few moments after the current is turned on, and the temperature may be held between that of the laboratory and the melting-point of platinum with great precision. The temperature within the muffle tube can be ascertained, of course, by the method depending upon the melting-point of pure metals, or by exploring the interior of the furnace with a platinum loop carrying an electrical current, in connection with the proper electrical
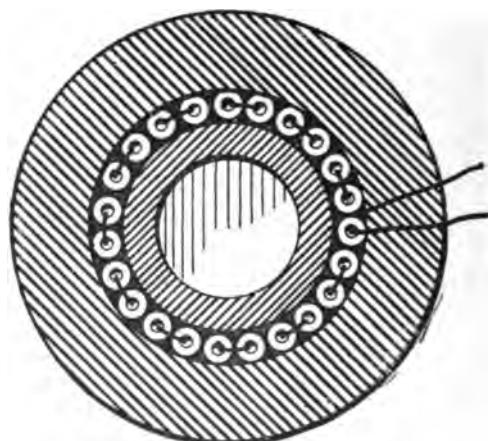
FIG. 96.—Top View of a Vertical Type of Wire Resistor Furnace.

instruments. A hint of practical value may not be out of place at this time. With certain kinds of fire-clay material there is shrinkage upon the first firing, and the platinum wire, because of its own expansion by heat, is apt to come out of the threaded groove, causing the separate convolutions of the adjacent coils to come into contact and cause serious trouble by short circuiting. This may be avoided by rewinding the furnace after the shrinkage has taken place, winding on the platinum wire quite tight, when there will be no more difficulty from this source.

Another design of furnace of the platinum-wire resistor type, is depicted in Figs. 96 and 97. The former being a top view looking down into the furnace which is of a vertical type. Here we have

a number of small tubes or pipe-stems arranged around the interior
of a thick outer casing of fire-clay and held in position by a fire-
clay plug fitting snugly in between them and by the lacing back
and forth of the platinum-wire resistor.   The second illustration
here shows a section through the vertical type of furnace. . With this
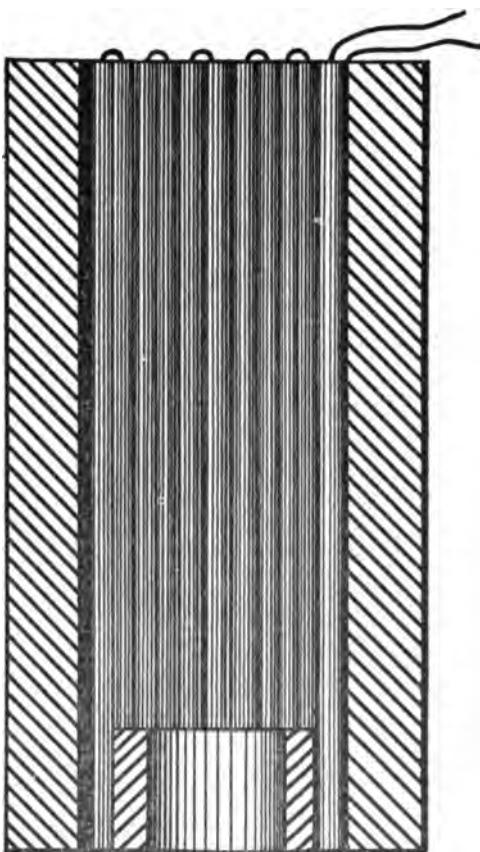
FIG. 97.—Section Through a Vertical Type of Wire Resistor Furnace.

design the platinum wire may expand without the slightest danger
of short circuits being formed, because it is entirely enveloped within
these small vertically and cylindrically arranged pipe-stems or
tubes.   In experimenting with the platinum wire winding of an
electric furnace to ascertain its maximum current-carrying capacity,

it must be borne in mind that the maximum current-carrying capacity of a platinum wire is very dependent upon its surrounding conditions. If we ascertain the current-carrying capacity of the platinum winding without the muffle tube in place and then give the coil the same current after covering with the muffle tube, we will, without question, burn out the furnace, for the reason that the heat can no longer dissipate so freely. It has been found in practice with a furnace of the general character of either of the foregoing designs that a platinum-wire coil will stand only about one half as much current when the muffle is in place as it did when freely exposed to the air. One must regard these resistor furnaces purely as convertors, as stated at the opening of the chapter, and we must maintain our furnace in operation at such a point, where the energy supply as electricity is carried off as heat energy, the balance between the supply on the one hand of electrical energy and the liberation of heat energy on the other hand, taking place within the limit of the melting-point of platinum. Because of the melting-point of platinum, this design of furnace is limited for work·under about 1600° C. But this vertical type may be so modified as to allow of the temperature being carried up to the very melting-point of the fire-clay itself, enabling the experimentor to melt down platinum, gold, iron, and steel. For this purpose this vertical pipe system of tubes must be packed with finely granulated carbon, and instead of being connected in series must be joined in multiple-arc by connecting all the lower ends together by means of a carbon disk, as well as the upper ends by means of a similar carbon disk. Such a modified furnace will, of course, require a very much heavier current to operate it, but the suggestion is made here for the benefit of those who may wish to experiment with small muffle furnaces at exceedingly high temperatures. For the production· of electrical products requiring extremely high temperatures a furnace of very different design must be employed. Although at the opening of this chapter the author classified all electrical furnaces on the principal of suitable resistors, the type of furnace we are about to describe is sometimes considered to be of the arc type. Although we may have an arc it may still·be maintained that this type ·of furnace is on the resistor principle, for in the present case the resistor consists of a stream of incandescent gaseous carbon. A very convenient

laboratory or lecture-room furnace for the production of such bodies as calcium carbide, is illustrated in elevation by the photograph
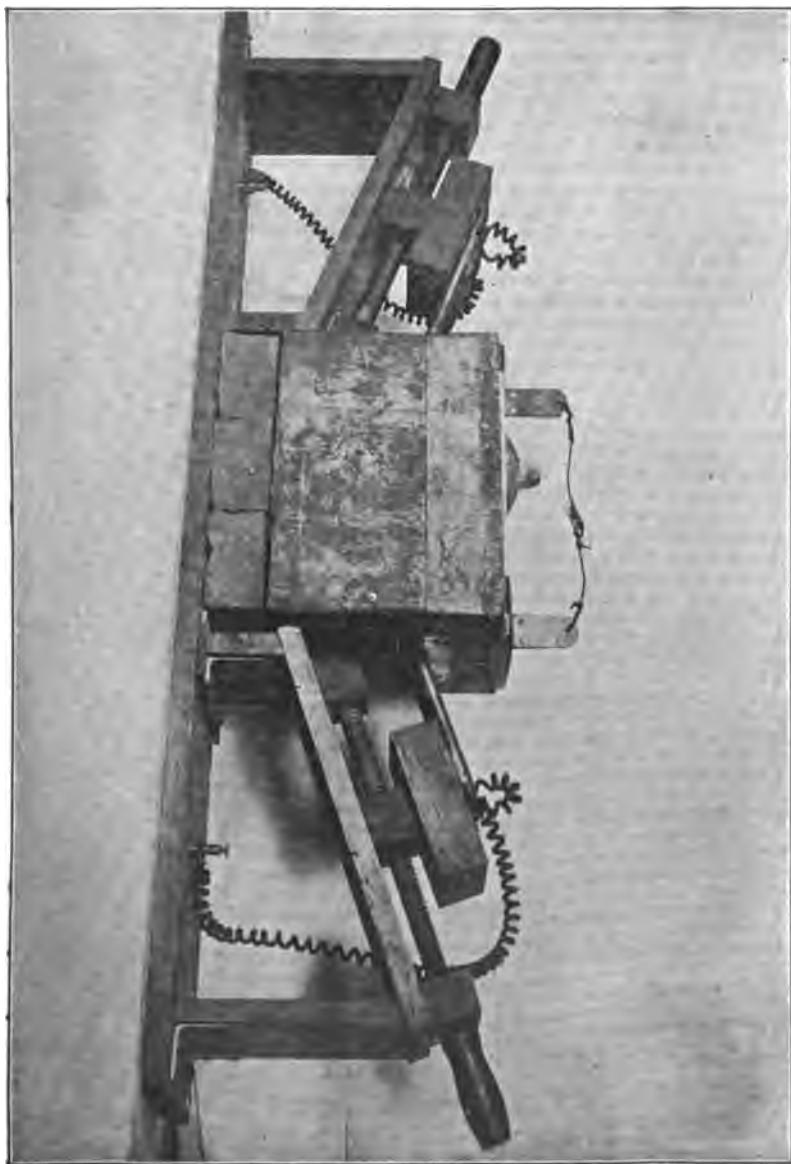
FIG. 98.—Elevation of Author's "Series Carbon Electric Furnace" for High Temperatures.

constituting Fig. 98. With this practical design of furnace, which was gotten up several years ago by the author, calcium carbide

may be produced on the lecture table in a very few minutes by drawing only about 20 amperes from a 110-volt lighting system.
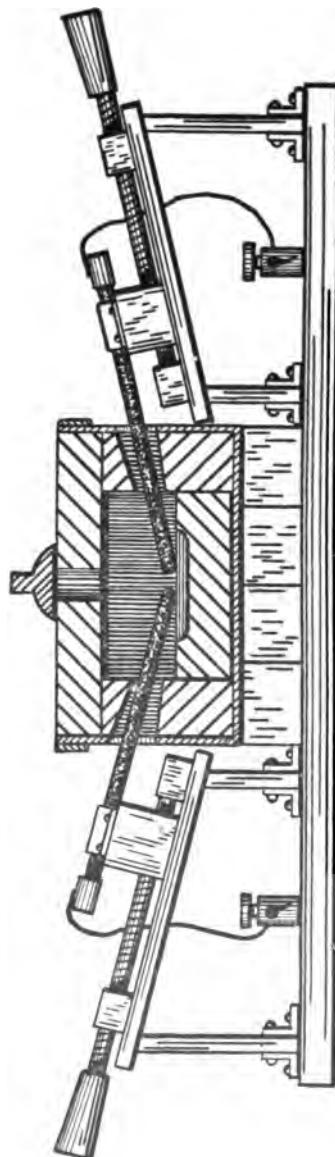
FIG. 99.—Section through "Series Carbon Electric Furnace."
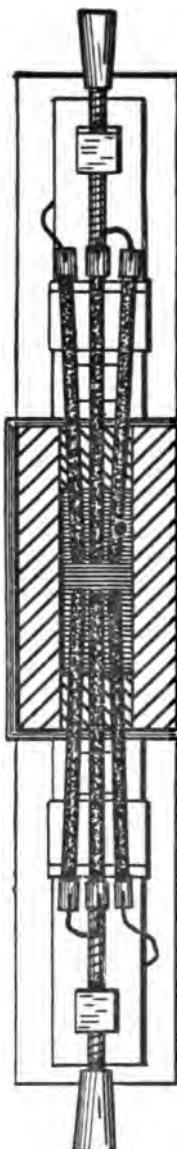
FIG. 100.—Top View of "Series Carbon Electric Furnace" with Cover Removed for Inspection of Arcs.

Fig. 99 represents a sectional view through this furnace, but it is only by referring to Figs. 100 and 101 that the peculiar design

of the furnace is understood. Here we have 6 carbon electrodes so connected that we have three electric arcs in series, allowing of the use of this furnace on incandescent lighting systems, protected only by a fuse of moderate capacity. It occurred to the writer a number of years ago in wiring a couple of arc lamps across the feeders of an incandescent lighting system, that a small experimental electric furnace could be gotten up on this plan. Only four carbons
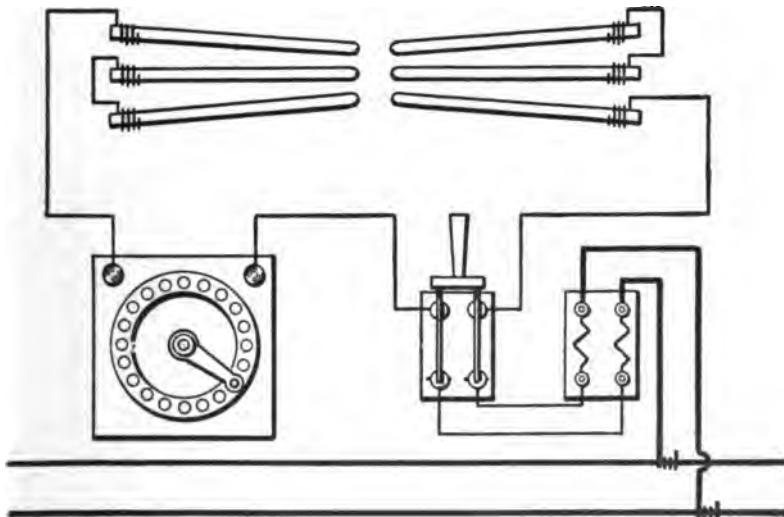
FIG. 101.—Diagram Showing Connections and Mode of Controlling Series Carbon Furnace.

were employed at first on the principle of the two arc lamps in series, but it was found upon the addition of such a charge of lime and coke as is utilized in the production of calcium carbide that it had a decided short circuiting effect and allowed too heavy a current to flow through the furnace. An additional pair of carbon electrodes were then added, giving three arcs in series instead of two. With such a furnace a suitable charge for the production of calcium carbide may be employed, but the resistance to the passage of electric current is not that offered by the three small arcs, but considerably less, as will be appreciated by any one familiar with electricity. The resistance is sufficiently high, nevertheless, to

enable óne to produce càlcium carbide in considerable quantities on 20 amperes of current.

Fig. 101 illustrates the connections of these series carbon furnaces
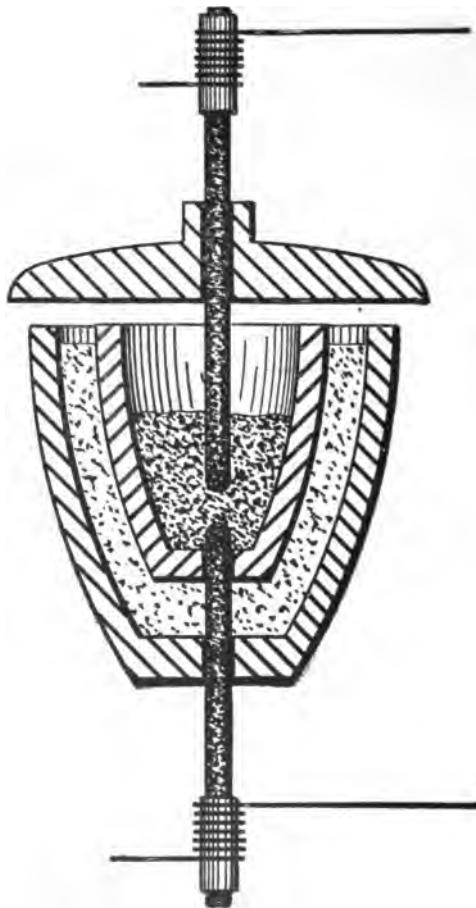
Fig. 102.—Vertical Type of Furnace with a single Arc.

coupled with a variable rheostat for controlling the intake of current by the furnace. If, however, ample current is at hand, say 50 or 60 amperes, a double crucible furnace, like that illustrated in Fig. 102, is found very convenient. Here we simply have two cru-

cibles, one within the other, separated by some good non-combustible heat insulating material. With this equipment, calcium carbide, carborundum, etc., may be prepared on a small scale. For the reduction of metallic oxides in the presence of carbon this type of furnace is most convenient. For the production of quantities of calcium carbide on a small scale on the lecture table the following directions should be carefully followed: Good unslacked lime and hard carbon are weighed out in the requisite combining proportions. The following equation indicates theoretically the production of calcium carbide, and from the same, the amounts to be weighed out may be learned·

$$CaO + C_3 = CaC_2 + CO.$$
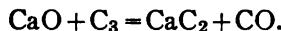
By hard carbon, it is meant that charcoal be not employed, for because of its lightness it is apt to burn away without combining with the calcium of the lime. A convenient and most satisfactory carbon is obtained by crushing up in a large mortar fragments of old electric light carbons. Both the carbon and the lime should be ground to a fine granulation and intimately mixed together, and for this purpose the writer has found an old iron coffee-mill to meet the requirements in a most satisfactory manner. After a run of half an hour at a full incandescent temperature, fragments of calcium carbide will be obtained as large as an English walnut, which yield a large supply of gas, and may be burned in a large jet if thrown into a cylinder jar of water equipped with a small glass outlet tube and tight fitting stopper. As we experiment with hydrogen the jet should not be lighted until one is sure that all of the air has been driven from the cylinder. It must be remembered that the preparation of calcium carbide requires extreme temperature. The furnace must be allowed to be well under way in temperature before the timing of the run is begun. An electric furnace of this type is nothing more or less than a box of poor heat conducting material, in which electrical energy is poured, so to speak, until the entire interior assumes a temperature of the electric arc. The temperature of the arc has been carefully computed by many experimenters and is found to be in the neighborhood of 3500° C., which is 6332° F. We will not go into the commercial question of electrical furnaces

here as it would constitute a treatise in itself.   We are, nevertheless, fully enabled at this time and at this stage of our work to conduct an efficiency research upon electrochemical processes of this kind, if we have profited by the previous chapters on the theoretical side of our subject.   Believing that we have here outlined the simplest types of electric furnace available for experimental work, we will take up another subject in the next chapter.

CHAPTER XV.

PREPARATION OF ORGANIC COMPOUNDS.

THE ELECTROLYSIS OF SODIUM ACETATE.

In the present chapter we will produce electrolytically certain organic chemical compounds, and we will start our work by taking a typical case of organic electrolysis and one of peculiar beauty for demonstration purposes, as a combustible gas is set free at each electrode. To accomplish this we will electrolyze a strong solution of sodium acetate: $CH_3.COONa$ in the assembled apparatus, as illustrated in Fig. 103. Here we have at A the electrolytic cell, which consists of a wide mouth glass cylinder, carrying a large rubber stopper. Through the center of this rubber stopper is a glass tube of large diameter terminating in a bell mouth, as shown at B. This glass tube, which is somewhat the shape of a lamp-chimney, is provided with a tight fitting stopper at its top through which passes the wire attached to the anode and the glass tube C, leading to the wash-bottle F and gas-collecting tube D at the extreme left. Immediately under the bell-mouth opening of the tube B is a cylindrical porous pot E containing the anode G, which is of platinum. The cathode H is a large cylinder of pure sheet copper surrounding the porous pot E and leaving considerable space for electrolyte between it, the walls of the outside containing vessel and the porous pot. The tube I passes through the stopper of the outside container, the electrolytic cell A and runs to the bottom of the wash-bottle J, thence to the vertical gas collecter K. The wash-bottle J contains plain water, whereas wash-bottle F contains lime-water for the absorption of carbon dioxide. The terminals of the electrolytic cell are connected to the lighting system through our lamp-bank and two or three 16-c.p. lamps will suffice for the

current. At the cathode we will have two atoms of hydrogen isolated, as a result of the setting free of sodium, as shown by the
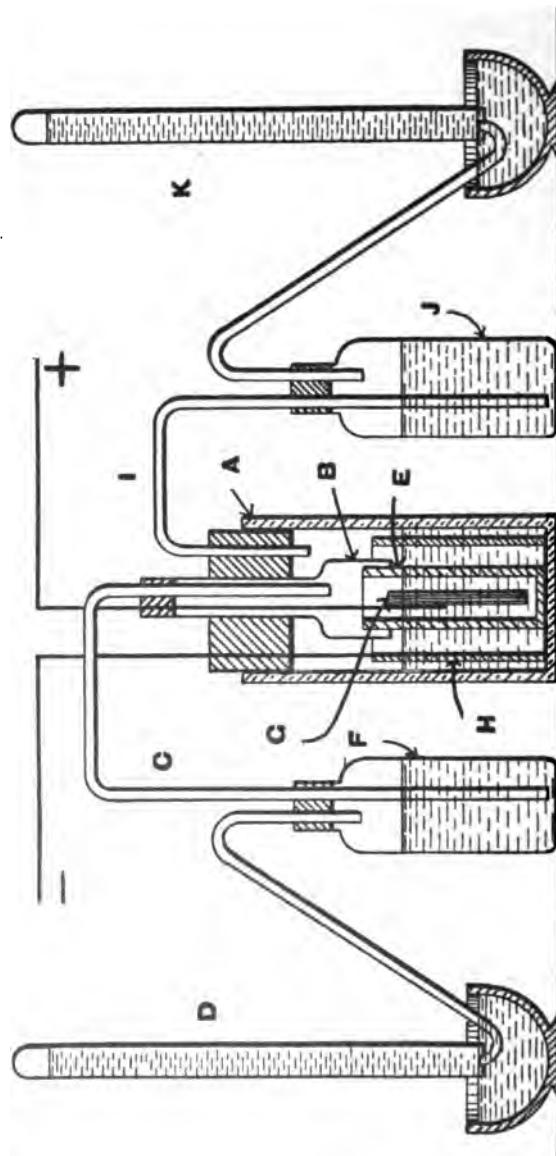
FIG. 103.—Apparatus for the Experimental Electrolysis of Sodium Acetate.

secondary reaction in the following equation:

$$2Na + 2H_2O = 2NaOH + 2H.$$
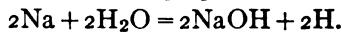
This hydrogen will, of course, be collected in the tube K after passing through the wash-bottle J. At the anode the following processes take place:

$$2CH_3.COO + H_2O = 2CH_3.COOH + O,$$
$$2CH_3.COOH + O = C_2H_6 + 2CO_2 + H_2O.$$
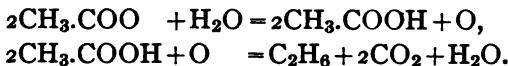
The gas ethane C_2H_6, and carbon dioxide CO_2 escape through the tube C. The carbon dioxide is absorbed by the lime-water with the formation of calcium carbonate, whereas the ethane collects in the vertical tube D. It is interesting to note that the volume of ethane is about the same as the volume of hydrogen produced. According to Jahn, we would obtain more ethane if it were not for the oxidation of some of the acetic acid at the anode by the oxygen, as suggested by the following equation:

$$CH_3.COOH + 4O = 2CO_2 + 2H_2O.$$
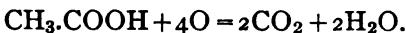
The hydrogen and ethane produced may be ignited to show that both gases are of a combustible nature.

THE ELECTROLYTIC PRODUCTION OF IODOFORM.

For the production of iodoform we will require a beaker of about 500 cubic centimeters capacity, a cylinder of nickel wire gauze to serve as cathode, a porous pot and a suitable platinum anode. The beaker is to be mounted upon a tripod in order that the process may be conducted at an elevated temperature. Free iodine when allowed to react with a heated aqueous alkaline solution of ethyl alcohol produces iodoform, (CHI_3.) Fig. 104 shows the assembled apparatus with a thermometer for observing the temperature of the reaction. The nickel gauze cylinder, porous pot, and anode are also separately shown at the right in this illustration. Without taking into account the intermediate products formed, the reaction may be expressed very simply by the following equation:

$$CH_3CH_2OH + 10I + H_2O = CHI_3 + CO_2 + 7HI.$$

One will observe that we have hydriodic acid formed, which, of course, will combine with the sodium hydroxide present to produce sodium iodate and carbonic acid. The following directions for the actual carrying out of an experiment may be followed to advantage: The cathode of nickel-wire gauze is placed in the beaker,

together with the cathode liquid, which consists of a strong solution of sodium hydroxide. Within the porous pot, which is next placed in position is a solution consisting of 15 grams of sodium hydroxide, 10 grams of potassium iodide, 10 cubic centimeters of ethyl alcohol, and 100 cubic centimeters of distilled water. The thermometer is
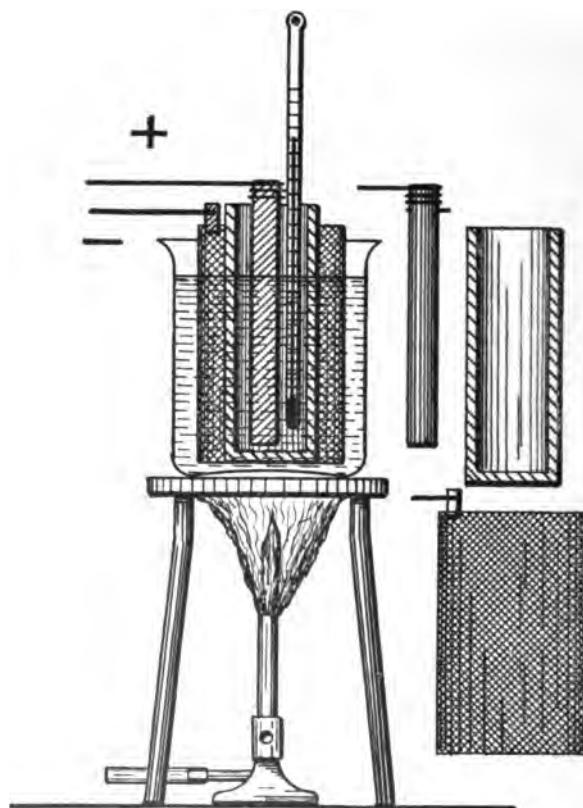
FIG. 104.—Apparatus for the Electrolytic Production of Iodoform.

placed within the porous pot and the temperature elevated to about 70° C. The best working current density at the anode for this preparation is about one ampere per square decimeter. It is well to allow the current to run for 4 hours, when the process may be interrupted. The liquor from the interior of the porous pot is poured out into an evaporating dish, when after standing for some

time, from 1 to 2 hours, a beautiful crystalline deposit of iodoform is filtered off and allowed to dry at the temperature of the laboratory. There will be formed as a secondary product in the mother liquor, sodium iodate. The yield of iodoform is about 70 per cent. This is a very satisfactory organic preparation, and lends itself to some interesting efficiency determinations when conducted in connection with suitable electrical measuring instruments.

THE ELECTROLYTIC PRODUCTION OF CHLOROFORM.

Chloroform may also be prepared electrolytically. For this purpose a suitable still, which may be heated by a steam jacket and containing a set of revolving paddles, is employed. These paddles consist of carbon plates and are made the anode in the electrolytic process. The interior of the still, which must be of lead, serves as cathode. A 20 per cent solution of common salt is placed in the still to which acetone is admitted from the bottom, as shown, by means of the tube which leads to the elevated reservoir. The acetone is converted into chloroform by the combined action of chlorine and sodium hydroxide. The reaction may be theoretically illustrated in two stages according to the following equations:

(1) $(CH_3)_2CO + 3Cl_2 = CH_3COCCl_3 + 3HCl;$
Chloracetone.

(2) $CH_3COCCl_3 + NaOH = CH_3COONa + CHCl_3.$
Sodium Acetate.   Chloroform.
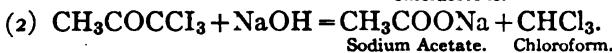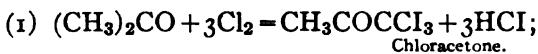
The chloroform produced distils off because of the elevated temperature maintained by the live steam and is collected in a suitable receiver. It is claimed that from 100 parts by weight of acetone 180 parts by weight of chloroform are produced. The theoretical yield figures out 206 parts by weight of chloroform, so it will be seen that the process is quite economical. It is interesting to note from a study of these equations that only one of the two available methyl groups in the acetone is utilized for the production of chloroform. In the drawing, Fig. 105, it will be observed that the current is sent into the revolving anodes by means of a brush and the commutator.

THE PRODUCTION OF ACETYLENE.

There is to-day a big field for the organic chemist with reference to electricity. Some of the reactions brought about by the

aid of electricity possess the greatest field for synthetic organic chemistry. Berthelot showed that carbon and hydrogen combined to form acetylene on causing the electric arc to pass between carbon electrodes in an atmosphere of hydrogen.

$$2C + H_2 = CH \equiv CH.$$
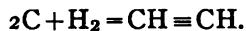
For this purpose a glass globe was employed with two openings opposite each other in the form of tubulures, into which were fitted
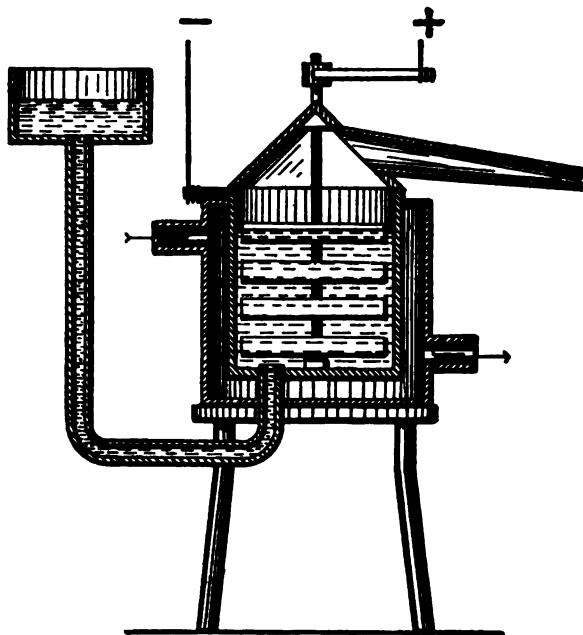
FIG. 105.—Apparatus for the Production of Chloroform Electrolytically.

large stoppers carrying electrodes and entrance and exist tubes for the gas. The globe was first carefully swept free of air by a current of hydrogen when an electric arc was established through the carbon pencils within. A good yield of acetylene results from such a combination. This is, of course, simply of scientific interest and has no practical application. The following organic synthesis, however, is not only of scientific interest in the experimental labora-

tory, but has found a commercial application.   It pertains to the production of carbon disulphide in the electric arc.

THE PRODUCTION OF CARBON DISULPHIDE.

If, instead of supplying hydrogen to the enclosed electric arc between carbon electrodes, we supply sulphur or roll brimstone we get quite another product, namely: The mobile and volatile liquid, known as carbon-disulphide. This interesting compound may be prepared upon an experimental scale by assembling and operating such a piece of apparatus as illustrated in Fig. 106.   Here
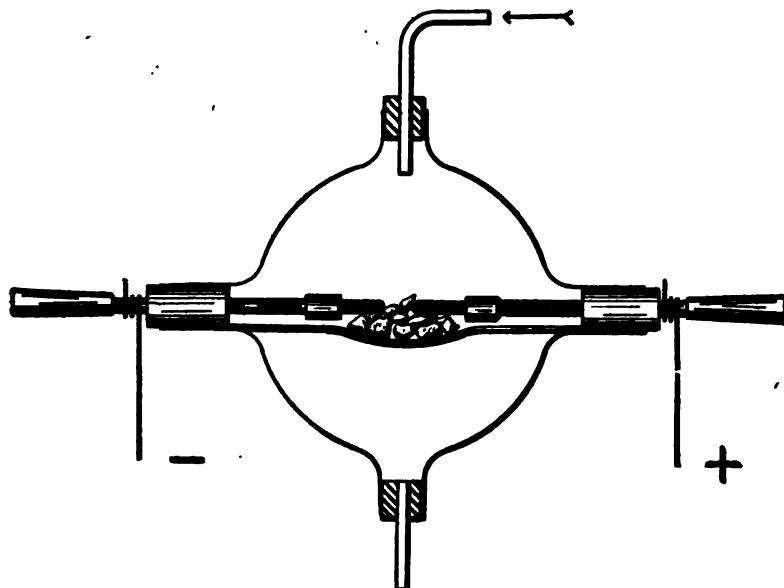
FIG. 106.—Glass Globe, Carbon Electrodes and Sulphur for the Experimental Production of Carbon Disulphide.

we have a large glass globe equipped with four tubulures or necks to receive stout stoppers.   A metal rod with insulating handle passes, as indicated, through two of these tubulures in a horizontal position, terminating in holders for supporting carbon pencils.   Before these stoppers are put in place a narrow strip of thin asbestos is drawn through and held in position as a bridge by the stoppers which carry the electrodes.   Upon this piece of asbestos, between the ends

of the carbon electrodes, the roll brimstone is placed. The globe is swept out by carbon dioxide gas and the arc is started between the carbon pencils. Carbon disulphide in the state of a gas is formed within the arc, condensing in minute drops over the interior surface of the glass globe. After a suitable run, enough carbon disulphide will condense to run to the bottom of the globe, where .
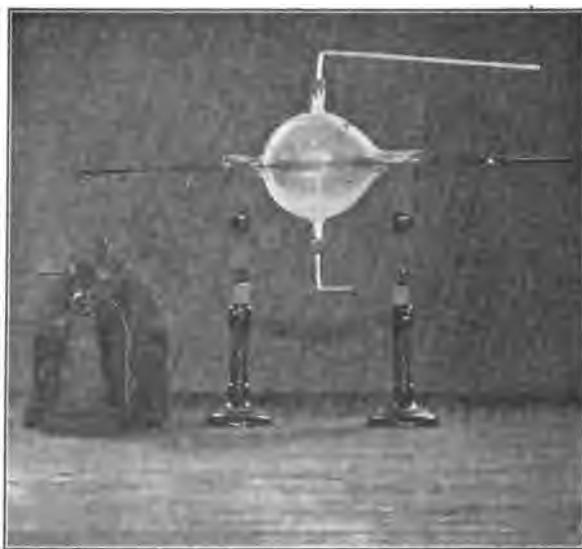
FIG. 107.—Experimental Equipment Complete for the Preparation of Carbon Disulphide.

it flows out through the bottom opening and may be collected in a test-tube. So much for the experimental side of this work. It will be of interest to know that this process is being carried on upon a commercial scale in New York State where specially designed furnaces are in operation. These furnaces, erected at Penn Yan, are 16 feet in diameter and 41 feet high. The process as carried on by Taylor originally consisted in building a furnace with an experimental shell of iron, in which the brimstone is placed and melted down by the heat radiated from the inner metal shell of the furnace where the electric arc had been maintained. Brick walls were subsequently substituted for those of metal and the sulphur in the cold state fed directly to the furnace surrounds the interior

so completely as to practically make a blanket, which, in melting, carries back into the furnace the heat absorbed. This regeneration proved to be efficient in the extensive production of carbon disulphide. It is said that in a building containing the furnace there are no unpleasant gases that are in the least in evidence, the entire building being at times as comfortable as any ordinary; manufacturing plant; in fact other operations could be conducted within the same building without inconvenience. Arrangements were made in this process to keep the electrodes constantly and automatically supplied with broken carbon which provides the electrodes, themselves of carbon, with large contact surface, from which the broken carbon tapers off to the interior of the furnace where the current resistance converts the electrical energy into heat just where it is required for effective work. The sulphur rises in the bottom of the furnace, and its heat is regulated by feeding cold sulphur into the surrounding chamber to meet the requirements. The sulphur, being a non-conductor of electricity, itself plays an important part in regulating the amount of current which flows through the furnace. The alternating current is used in Mr. Taylor's furnace, which has practically revolutionized the manufacture of carbon disulphide in America.

ELECTROLYTIC OXIDATION.

THE PREPARATION OF KANARIN.

As we learned in a previous chapter, oxidation and reduction may be effected by the proper adjustment of current density, etc., and we will now apply this important electrolytic oxidation method for the practical production of certain organic oxidation products. Organic electrolysis may, in the majority of cases, be divided into two general processes entirely independent of current density conditions. On the one hand we will have oxidation, and on the other we will have reduction. Therefore, most cases of organic electrolysis are either oxidation or reduction processes. The electrolysis of organic compounds is of comparatively recent development, and a sound knowledge of organic chemistry is essential for work in the new field of organic electrochemistry. It would be impossible in a

general experimental work on this subject to go deeply into the chemistry and electrochemistry of organic oxidation or reduction products, and we will content ourselves by introducing one or two experiments which illustrate the effect of the electric current upon organic compounds when applied under proper conditions. Perhaps the production of the organic yellow dye, known as kanarin, will serve best to illustrate a typical case of organic oxidation. For carrying out an actual experiment we will employ a Hoffman apparatus of a general type, which is shown by the photograph in Fig. 108. For this experiment the Hoffman apparatus is provided with platinum electrodes, and the electrolyte consists of a solution of potassium sulphocyanide in the proportion of one part by weight of the sulphocyanide, and five parts by weight of distilled water. This solution is placed within the Hoffman apparatus, the terminals of which connect through two or three 16-c.-p. lamps to the lamp-bank and 100-volt lighting system. Hydrogen is given off at the cathode and streams up through the solution in the cathode tube of the Hoffman apparatus, where it collects, as in the ordinary case of electrolysis of dilute sulphuric acid. The interesting optical feature of this experiment is the non-appearance of the corresponding oxygen at the anode. Here we have, therefore, hydrogen streaming off the cathode and collecting in the cathode tube, with no gas liberated at the anode, for the oxygen set free immediately oxidizes and combines with the sulphocyanide acid to produce kanarin, which appears as a yellow mass extending over the surface of the anode. The theory of this oxidation may be represented by the following equation:

$$6HCNS + 11O + H_2O = C_6H_4O_2N_4S_5 + H_2SO_4 + 2HNO_3.$$

The kanarin which, after fifteen or twenty minutes, will have collected in sufficient quantities for an experiment in dyeing, for which purpose the kanarin is dissolved in a basic solution.

CASES OF ELECTROLYTIC REDUCTION.

Let us now look into a case of reduction, and for this purpose we will choose nitrobenzene. The nitrobenzene is first dissolved in strong sulphuric acid and placed in a porous pot, into which a

platinum cathode is immersed. The anode, of platinum, is placed outside the porous pot in an 80 per cent solution of sulphuric acid in distilled water. The porous pot with its cathode and

FIG. 108.—Hoffman's Apparatus which Deserves a Special Place of Honor in Electrochemical Work.

the anode are placed within a larger beaker glass and the electric current turned on. The product is para-amido-phenol sulphonic acid of the following chemical composition: $C_6H_4(NH_2)(OH)$. The reaction within the cell is believed to take place in two stages,

as shown in the following equations with the intermediate production
of phenylhydroxylamine:

$$C_6H_5(NO_2) + 2H_2 = C_6H_5(NH)(OH)H_2O;$$
<div align="center">Phenylhydroxylamine.</div>

$$C_6H_5(NH)OH \quad = C_6H_4(NH_2)(OH).$$
<div align="center">Amido-phenol.</div>
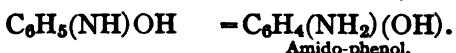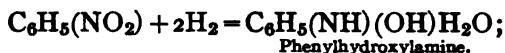
The ultimate product, which is para-amido-phenol sulphuric acid,
separates from the electrolyte in the form of fine crystals, which
are filtered off through asbestos. To illustrate the working range
of organic electrolytic reduction it may be well to refer to two other
preparations by the reduction of nitrobenzene. Nitrobenzene, when
in a diluted sulphuric acid solution, yields under similar conditions
of electrolysis, the aniline direct as shown by the following equation:

$$C_6H_5(NO_2) = C_6H_5(HNH_2) + 2H_2O.$$

When nitrobenzene is in an alkaline solution azobenzene is produced,
as shown by the following equation:

$$2C_6H_5(NO_2)H_8 = C_6H_5NNC_6H_54H_2O.$$

Such reductions may, of course, be brought about by ordinary
chemical means, but with the electrolytic process, there are many
outside points in its favor, among which may be mentioned an
ease of control of the course of the reaction. There are, however,
cases where electrolytic reduction brings about results different
from those obtainable by ordinary chemical means. It will now
be seen from the fundamental and typical cases given here, that
oxidation and reduction in cases of organic electrolysis do not
depend so much upon conditions of current density at anode or
cathode, but more especially upon the composition of the electrolyte
itself. The cases that might be here cited in the field of organic
chemistry are almost without limit, and we must content ourselves
in the present work with the typical cases presented.

CHAPTER XVI.

THE PRIMARY CELL.

IN the present chapter we will deal with the production of the electric current through chemical action, and this phenomenon may be regarded as the converse of what we have hitherto considered. We have, up to the present time, applied the electric current to compounds in a state of solution, and we will, in the present chapter, look into the production of the electric current by the chemical action of substances in solution within a suitably arranged and assembled cell. Two great problems in electrochemistry presented themselves to the early workers in this field, the first being: How does the electric current decompose electrolytes and what is the mechanism of such decomposition, which we term electrolysis?

The second problem relates to the origin of the electric current. What produces it, and how can we satisfactorily explain the phenomena observed when, for example, dissimilar metals are immersed in an acid? We have already considered, at considerable length, the decomposition side, or electrolysis, when compounds are subjected to the influence of the electric current.

In our very first chapter we touched upon the origin of the electric current in a general way and referred to the work of Galvani with his frogs, and also to Professor Fabroni, of Florence, as well as to Alexander Volta, of Pavia. For the sake of historic interest, and also to illustrate to the student the hopeless condition of affairs pertaining to the origin of the electric current, we will turn for an instant to the time when Galvani and his famous experiments upon frogs attracted the attention of the scientific world. It will be remembered that in the famous experiment of Galvani, conducted in the year 1786, the dawn of dynamic electricity was marked. It is true that six years prior to this, Galvani observed

that the limbs of dead frogs when hung upon a copper hook in the neighborhood of a frictional electric machine contracted violently at each spark or discharge of the then known static electricity. It is the later experiment, however, conducted in 1786, which we may refer to as the first to attract universal attention. It will be remembered that Galvani obtained the twitching of the limbs of dead frogs without the agency of any electrical machine whatever, by bringing a copper wire joined to a nerve in contact with a piece of iron wire, which was attached to one of the limbs of the frog. The analogy of these results, although six years apart, nevertheless impressed upon Galvani the belief that the two distinct phenomena were due to one and the same cause, namely: that of electricity, and he described his discovery of what he styled "animal electricity" in his celebrated memoir, "De Viribus Electricitatis," in 1791. A complete history of the voltaic cell and its origin would debar us, for lack of space available here, from considering, as we must, the later theories and the more experimental and practical side of the electric battery. To give an idea, however, of the hopeless state of affairs existing until the theory of electrolytic dissociation threw some light upon the subject, we will refer to the views of Sturgeon who, writing on the subject of Voltaism in 1842, expressed himself as follows: "Voltaism is the production of electricity by the association of metals and other inorganic bodies by the simple contact of inorganic bodies, whether solid or fluid." Galvanism is the production of electrical currents, "either by a natural or artificial association of animal matter, whether alive or dead." The "animal matter" element of this definition was eventually abandoned by most of the investigators, when two distinct theories were formulated, namely: "The contact theory of the cell" and the "chemical theory of the cell." De la Rive, writing in 1853, defined the voltaic cell in the following words: "An apparatus in which electricity is developed, according to some, by the contact of two metals of a different nature, and according to others, by the chemical action of the liquids with which it is charged upon one of the two metals which enter into its formation." Faraday expressed himself upon these two theories of the cell as follows: "The contact theory assumes that when two different bodies being conductors of electricity are in contact, there is a force at the point of contact by which one of the bodies gives a

part of its natural portion of electricity to the other body, which the latter takes in addition to its own natural portion; that, though the touching points have thus respectively given and taken electricity they cannot retain the charge which their contact has caused, but discharge their electricities to the masses respectively behind them; that the force which at the point of contact induces the particles to assume a new state cannot enable them to keep that state; that all this happens without any permanent alteration of the parts that are in contact, and has no reference to their chemical forces."

"The chemical theory assumes that at the place of action, the particles which are in contact, act chemically upon each other and are able, under the circumstances, to throw more or less of the acting force; that, in the most favorable circumstances, the whole is converted into dynamic force; that then the amount of current force produced is an exact equivalent of the original force employed and that in no case can any electric current be produced without the active exertion and consumption of an equal amount of chemical force ending in a given amount of chemical change."

Gore writes upon the theory of the cell as follows: "The essential cause is the stored-up and ceaseless molecular energy of the corroded metal and of the corroding element of liquid with which it unites, whilst contact is only a static condition, and chemical action is the process or mode by which the molecular motions of those substances are more or less transformed into heat and current."

So much for these old theories. What have they taught us? Can we, in the light of them, satisfactorily explain the cause of the electric current, its origin, or birth? What must we do in order to produce the electrical current by chemical action? In the light of our chemical knowledge, let us see what takes place in the production of electricity in the following simple experiment: A little dilute sulphuric acid is placed in a beaker glass and two strips of metal of dissimilar character, for example, platinum and zinc, are partly immersed in the liquid so that they do not touch each other. If now the uppermost ends of these metal strips be joined by a suitable wire, an electric current in the direction from the platinum to the zinc will be produced, as may be proven by a magnetic needle or galvanometer. Bubbles of hydrogen may be seen to make their appearance on the surface of the immersed platinum strip. So much for the physical

manifestation. What can we say of the chemical? As general chemists, we can merely analyze the solution and weigh the metal strips for information relative to their loss or increase in weight. If we analyze the diluted sulphuric acid solution we will find that it is no longer merely a sulphuric acid solution, but that we also have zinc sulphate present, and that the strip of zinc has lost in weight, whereas the platinum is unaltered. An electric current has been produced. What was its origin and how can we, as physical chemists, explain its production? Before the advancement of the theory of electrolytic dissociation this was a matter veiled in great obscurity. We could, of course, say that the electric current was the result of chemical action, or that it accompanied the formation of sulphate of zinc, or that it was produced when zinc was dissolved in sulphuric acid, but does this really take us as deeply into the inquiry as we wish to go? In order to comprehend the modern theory of the cell, as based on the theory of electrolytic dissociation, we must know something concerning the solution tension of metals in addition to facts in connection with the theory of electrolytic dissociation. The solution tension of metals when immersed in liquids may be compared with the vapor tension of liquids. When a bar of metal is immersed in a liquid it tends to dissolve, and does dissolve to a greater or less extent. When, on the other hand, for example, an open vessel containing a liquid is placed in the laboratory, the liquid tends to evaporate and does evaporate to a greater or less extent. A bar of common zinc will dissolve in dilute sulphuric acid much more rapidly than a bar of iron, and, on the other hand, an open vessel of ether will evaporate much more rapidly than a similar vessel of water. We may term the tendency of the zinc to go into solution, the solution tension of zinc, and the tendency of iron to go into solution, the solution tension of iron, and from the fact that they go into solution at different rates, we may logically deduce that they have different tendencies to go into solution, or, in other words, we may say that they have different solution tensions. We will, a little later in this chapter, take up the experimental determination of the solution tension of metals. We will see, when we come to this work, that we have means for quantitively measuring and comparing what we now term the solution tensions of the metals. We can at a fixed temperature establish a solution tension value for any metal in

a given liquid, as we can measure the vapor pressure or tendency of a liquid to volatilize at a given temperature. A most important fact for us to take into account at this time is the fact that the solution tension of any metal immersed in any given liquid is indepen-
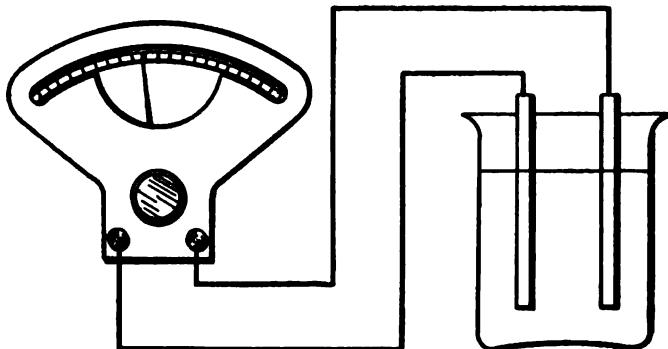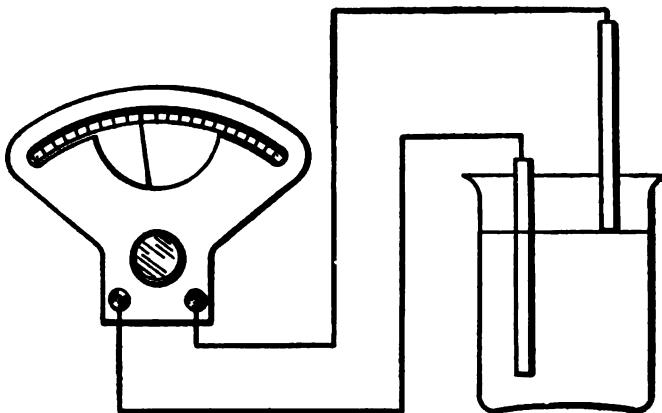
FIG. 109.—Experiment to show that Solution Tension is Independent of Surface Area.

dent of the size of surface of the metal immersed, which, we will see is the case as indicated by E.M.F. phenomena, if we perform an experiment as indicated in Fig. 109. We know, and can experimentally demonstrate that the vapor pressure of ether, for example, is independent of the surface exposed under the same conditions of temperature and barometric pressure. For experiment with vapor tensions the reader is referred to any good text-book on

experimental physics. As we will presently see, we may arrange the known metals in a series, in the order of their solution tensions, and such a table of the metals may be referred to in reference to a liquid or electrolyte as the tension series of the metals. This preliminary outline has been necessary, in the opinion of the writer, before presenting to the student the following experiment, which, upon the basis of the theory of electrolytic dissociation, explains in a beautiful and satisfactory manner the origin of the electric current in the voltaic cell.

The experiment to which we now refer has been styled by Ostwald and others, "Chemical Action at a Distance." Ostwald presented a paper in 1891 entitled, "Chemische Fernewirkung." An exceedingly interesting point to which Ostwald draws attention is the fact that amalgamated zinc is not dissolved by dilute acids. It has also been pointed out that chemically pure zinc will not dissolve in dilute acids. This will appear to those familiar only with general chemistry to be a remarkable statement. The general chemist, without a knowledge of physical chemistry, will find it difficult to believe that sulphuric acid, for example, will not dissolve a stick of zinc if the latter be chemically pure. If, on the other hand, the zinc is impure, that is to say, contains traces of other metal as alloy or other metals adhering or cast within or upon its surface, the zinc will dissolve with rapidity. It is quite well known in this connection, that in the preparation of hydrogen by throwing granulated zinc in dilute sulphuric acid that the evolution of the gas is greatly promoted by the addition of some scrap platinum or a few bright iron nails. Ostwald, in his writing concerning this very point, speaks first of wrapping a platinum wire around the top of a rod of zinc and immersing its lower end in dilute acid. If the rod of zinc is chemically pure there will be no appreciable chemical action if the free end of the platinum wire does not dip in the acid. If, however, the end of this platinum wire is immersed in the acid, the zinc will go into solution rapidly, and hydrogen will be liberated from the immersed end of the platinum wire. Ostwald also states that it is not necessary for the zinc to be surrounded by the platinum wire, for if such a wire touches the zinc at any point where it is immersed in the acid, solution will take place. It was also suggested that the zinc and platinum

wire be joined at one place and then the free lower ends of both zinc and platinum be immersed in a vessel containing, for example, potassium sulphate. A porous partition is placed between the immersed zinc and the platinum so that the electrolyte around the zinc is separated from the electrolyte around the platinum. Ostwald then asked the following question: "To which metal must we add sulphuric acid in order that the zinc may be dissolved?" This question, to the general chemist without a knowledge of certain fundamental principles of electrochemistry, would appear to be an absurd one, for it would seem to him to be very evident that the acid should be poured into the partition containing the zinc. If such an experiment is carried out we will find that in order to secure the solution of the zinc, strange as it may appear, the acid must be added to the compartment containing the platinum. When the zinc dissolves, a brisk liberation of hydrogen gas is observed from the platinum. This experiment is illustrated in Fig. 110 and consists of two beaker glasses containing a solution of
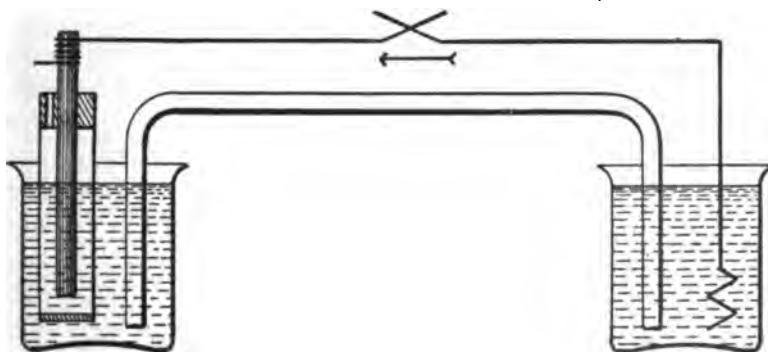
FIG. 110.—Experiment to Show "Chemical Action at a Distance."

potassium sulphate, joined together by a siphon-tube containing some of the same solution. In the left of our illustration may be seen a cell of glass, cylindrical in shape, on the pattern of an ordinary lamp-chimney, its upper end being fitted with a perforated stopper, as shown, carrying a rod of pure zinc. The lower end of this cylinder is tightly closed with vegetable parchment, simply to act as a porous diaphragm. In the present arrangement of two beakers

separated by a siphon-tube this precaution to prevent diffusion currents is not absolutely necessary. The glass cylinder carrying the zinc is, of course, also filled with the solution of potassium sulphate. A piece of platinum wire is wrapped around the top of the zinc bar, and a second piece, terminating in a spiral to give it more surface, is immersed in the distant beaker. If now a few drops of sulphuric acid be introduced within the cylindrical cell containing the zinc, there will be practically no solution of the metal. If, on the other hand, a few drops of sulphuric acid are poured into the beaker at a distance, and connected by the siphon containing the platinum coil, a brisk evolution of hydrogen will take place from this platinum wire, and after a few minutes the presence of zinc sulphate within the glass cylinder surrounding the rod of zinc may be proven by analytical means. In the drawing one will observe an arrow pointing toward the rod of zinc in the left-hand beaker, and just above the arrow the platinum wires are shown in contact. If after adding sulphuric acid to the right-hand beaker, as shown in the drawing, the liberation of hydrogen from the platinum spiral and solution of zinc in the left beaker is noted, we separate these platinum wires from contact, the liberation of hydrogen ceases together with the solution of zinc. Upon touching the platinum wires together again, however, the chemical action recommences, and if we bring a sensitive magnetic needle in the neighborhood of the platinum wire we will find that an electric current is flowing through it in the direction of the arrow, namely: from the right-hand beaker containing the platinum to the left-hand beaker containing the zinc.

The explanation of these phenomena is comparatively simple when based upon the theory of electrolytic dissociation. The source of the current in a voltaic cell may be, therefore, understood from the following consideration: When a rod of zinc is immersed in a solution of a neutral salt, potassium sulphate for example, zinc ions are sent off in solution because of the solution tension of the zinc. These zinc ions are driven into solution because of the solution tension of zinc in an analogous manner to the sending off of ether molecules into the air when an open vessel of ether is allowed to stand in the laboratory. In the case of the immersed zinc it is made negative in electrical sign, and the solution which

has received the ions, which are positive in sign, becomes itself positive. Thus solution continues until a difference of potential in solution is established. Again comparing the phenomena of vapor tension; ether in an open vessel would continue to evaporate until an equilibrium is established. In the case of the zinc rod immersed in the sodium sulphate solution, the number of zinc ions driven off, although very small, establish an equilibrium after a while. Referring once more to the case of the zinc rod in the electrolyte, the driving off of the zinc ions will cease after a certain point has been obtained, because of an excess of positive ions in the solution. In order that more of the zinc ions may be driven out some of these positive ions must be removed. If the zinc is connected with another metal, for example our platinum wire, such platinum wire, of course, takes the same negative charge as the zinc. When the negative end of this platinum wire, therefore, is coiled and immersed in the solution it attracts the excess positive zinc ions which exist in the solution. We might expect, from the description of the experiment as far as we have gone, that the zinc ions in the solution would be attracted to the platinum spiral, give up their charges and deposit thereon, or, in the case of potassium, decompose the water which is present with the liberation of hydrogen. The behavior in such a state of affairs depends upon, not only the nature of the ion, but of the electrode also. In such an experiment, with the positive ion, which is the potassium resulting from potassium sulphate, the difference in potential produced upon the introduction of the zinc is insufficient to cause the potassium ion to give up its charge to the platinum. If, however, a little sulphuric acid is added to the beaker at the right containing the platinum coil, and the wires are in contact, the difference in potential produced by introducing the bar of zinc is sufficient to compel the hydrogen to give up its positive charge to the platinum spiral and appear upon its surface as minute bubbles. The hydrogen ions in their becoming hydrogen atoms give up positive electricity to the platinum, neutralizing the negative charge which the latter carries. A current of electricity will then flow along the wire in the direction of the arrow, as indicated, to the zinc, which will, of course, become less negative than before the hydrogen separated at the platinum spiral, and the difference in potential between the zinc rod and the sur-

rounding solution becomes less. More zinc will, therefore, dissolve or be driven into solution as zinc ions. Additional hydrogen ions give up other charges to the platinum spiral and separate as gas, which, of course, in turn tends to make the zinc still less negative. Now, as long as we have the circuit closed, we will have an electric current, one from the platinum to the zinc as a result of the conversion of positive hydrogen ions to the ordinary hydrogen atoms. We have already referred to the fact that pure zinc does not dissolve in acids, while zinc which is impure displaces the hydrogen of an acid with readiness, or, as we may say in popular language, dissolves. The tendency of zinc, whether pure or impure, to go into solution is the same, only in one case it does and the other case it does not. Pure zinc, however, dissolves readily in an acid, or as we may say, technically speaking, displaces the hydrogen in an acid with avidity when in contact with some other metal of lower solution tension, such as platinum for example, immersed in the acid. The difference is not in the solution of the zinc, but is due to the ease with which hydrogen may escape from the solution. The presence of such a metal as platinum with a very low solution tension, allows the hydrogen to escape from its surface with ease, and upon this principle we may see why impure zinc dissolves in acids, when such impurities of low solution tension exist and act as points, or surfaces from which the hydrogen ions may discharge their electricity and escape as hydrogen gas. With a stick of impure zinc we have numerous impurities in the way of specks upon its surface of a lower solution tension than the zinc itself, and we will have a multiplicity of little galvanic circuits between the zinc impurities and through the electrolyte from the impurities to the zinc through the point of metallic contact. The reason why chemically pure zinc will not dissolve may also be ascribed to the fact that this metal itself has very high solution tension and sends its own positively charged ions into solution under a high solution tension opposing the tension of any other positive ions, like hydrogen for example, upon it. The rod of pure zinc will not dissolve in acids, therefore, because the hydrogen ions cannot give up their positive charges to it to escape as hydrogen molecules. As we saw by referring to Fig. 109, electromotive force is an exponent of solution tension, and from the experiment as depicted it may be seen that this solu-

tion tension is independent of the size or area of the metals immersed in an electrolyte. A difference in potential between the metal and the electrolyte is therefore established, which proves to be the fundamental origin of the E.M.F., produced in any given combination. We may ascribe the direct cause of this difference of potential to the solution tension of the metal which tends to drive ions from the metal into solution, making the metal itself negative in sign and the solution positive in sign, because of the presence of positively charged ions. It may be pointed out here that we also have a pressure in such a cell antagonistic to the solution tension of the metal, and this is the osmotic pressure of the solution itself, which tends to cause the ions driven out to separate on the electrode in the metallic condition. As a consequence of these opposing forces we have the formation of a double layer so to speak, and the difference in potential between the metal and the solution. This double-layer phenomenon is referred to in the electrochemical works as a Helmholtz double layer. Dr. Nernst very clearly describes the phenomena of the Helmholtz double layer in such a concise and lucid manner that it is deemed of value to the student to translate his own words upon the subject here. "Let us now consider what will take place if we dip a metal whose electrolytic solution tension is P into a solution of one of its salts; the osmotic pressure of the metal ions in this solution being p. Let at first $P > p$, at the moment of contact a number of positively charged metallic ions, driven by this large pressure, will pass into solution. Since by the latter a certain amount of positive electricity is carried from the metal into the solution, the liquid receives a positive charge, which arranges itself in the form of the positive ions contained in the solution on the surface of the metal. At the same time there is, of course, a corresponding amount of negative electricity set free in the metal, which also passes to the surface of the metal. We recognize at once that at the surface of contact of metal and electrolyte the two kinds of electricity must accumulate in the form of a double layer, whose existence, as is well known, was made probable some time ago by Von Helmholtz in an entirely different way.

"This double layer furnishes one component of force, which acts at right angles to the surface of contact of the metal and the electrolyte, and which tends to drive the metallic ions from the

electrolyte on to the metal, and thus acts in opposition to the solution tension. Equilibrium will be, of course, established when these two forces equalize one another. The final result will be the appearance of an electromotive force between the metal and the electrolyte, which will give rise to a galvanic current from the metal to the liquid, if by any device its existence is made possible.

" If $P < p$ the reverse of course takes place. Metallic ions separate from the electrolyte and are precipitated on to the metal until the electrostatic component of force of the positive charge of the metal and the negative charge of the liquid thus produced are in equilibrium with the excess of osmotic pressure. An electromotive force again appears between the metal and the electrolyte, which, under suitable conditions, gives rise to a galvanic current, but in this case opposite in direction to the case first considered.

" If, finally, $P = p$ the metal and electrolyte are in equilibrium at the first moment of contact; therefore, no difference in potential exists between the two."

In our practical and experimental work it is very important that we note quantitatively the potential differences existing between metals and solutions, and in order to practically determine this we will adopt the method involving a "normal electrode." This method employs the use of a previously prepared electrode, which has been termed a normal electrode, because its potential is known. This normal electrode is connected with a metal whose difference in potential we wish to ascertain and the E.M.F. of the entire system determined. As we know the potential of the normal electrode, that of the metal under examination is easily determined, the E.M.F. of the two when properly combined being the difference between the potentials on the two sides. The use of the normal electrode may be understood by referring to Fig. 111, where at the extreme left we have the normal electrode equipment, the beaker glass in the center containing the metal x, whose tension we are about to study, while at the right we have a sensitive standard volt-meter. The normal electrode equipment consists of a wide-mouth glass bottle containing a layer of purified mercury in the bottom, as indicated. On top of the mercury a layer of mercurous chloride is placed, and on top of this a normal solution of potassium chloride is poured. A platinum wire which passes through a pro-

tecting glass tube is suspended from the stopper, as shown. The wire is sealed in a glass tube in such a way that its lower extremity,

FIG. 111.—Use of a Normal Electrode in Determining the Electromotive Force of a Cell.
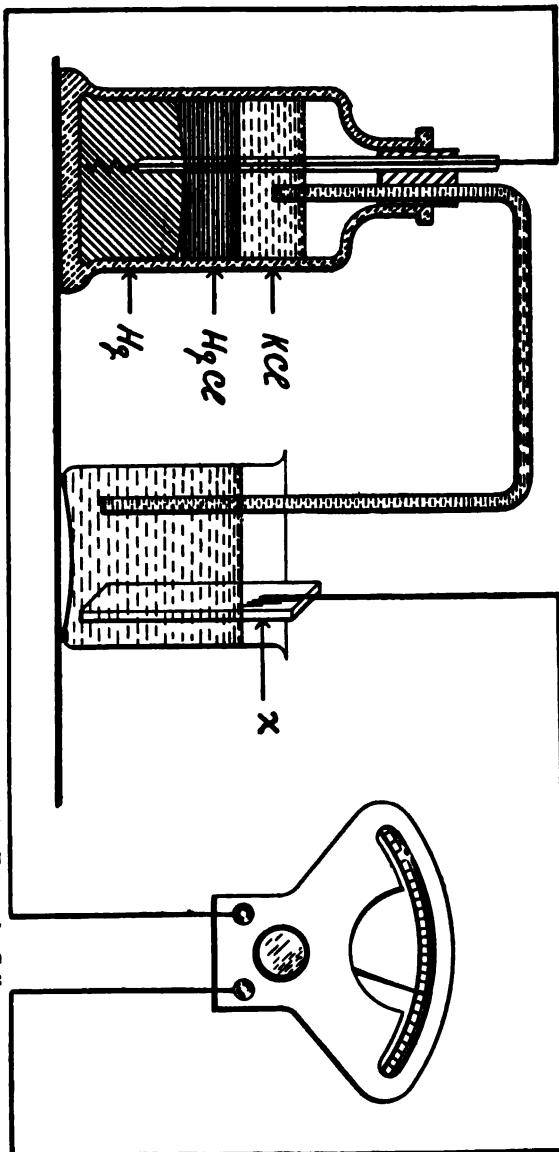
which is in the form of a tiny coil, comes into contact with the metallic mercury in the bottom of the bottle. A siphon-tube passes through

a second hole in the stopper of this bottle and dips in the normal potassium chloride solution, after having itself been filled with the same electrolyte. Connection is made with the mercury through the platinum wire, insulated by the glass tube, and this mercury serves as one electrode. The siphon is inserted in the liquid, whose
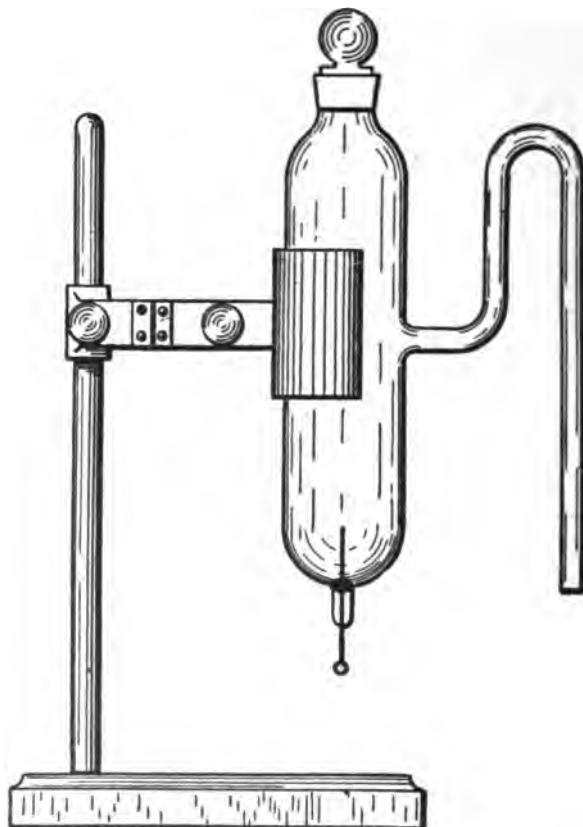
FIG. 112.—Special and Convenient Design of Normal Electrode.

potential against the metal under examination we wish to learn. The metal in question serves as the other electrode and is connected up with a sensitive volt-meter, as shown, and the E.M.F. of the entire system determined. The electromotive force between the mercury and the potassium chloride is .56 volt at the ordinary temperature of the laboratory. This .56 volt may be used as a constant for our

normal electrode, no matter what its size, if put together with chemically pure materials upon the plan as indicated. If the liquid in the beaker containing the metal, whose tension is to be measured, reacts chemically with potassium chloride, the solution of some indifferent compound may be interposed between the two. Fig. 112 shows a very neat and convenient design for a normal electrode. Here we have a glass vessel containing a platinum wire fused into its lower end to make contact with the mercury. The mercurous chloride is then put in position, as in the previous case, and the normal potassium chloride solution put on top and made to fill the siphon, which in this instance is fused into the side of the vessel. This form of normal electrode is conveniently held in an iron retort clamp as shown.

The following table is taken from the work of Neumann and represents the differences of potential between several metals and normal solutions of their salts.

Metal.	Chloride.
Magnesium.	1.231 Volts.
Aluminium.	1.015 "
Zinc.	0.503 "
Cadmium.	0.174 "
Iron.	0.087 "
Cobalt.	−0.015 "
Nickel.	−0.020 "
Tin.	−0.085 "
Lead.	−0.095 "
Gold.	−1.356 "
Platinum.	−1.066 "

We have learned that the solution tension of a metal is responsible for the difference in potential between itself and the electrolyte into which it is immersed. If we determine the potential difference and the value of the osmotic pressure of the positive ions in solution, we have the data necessary for calculating the solution tension of the metal.

A few common metals arranged in the order of their solution tension is given below, and this may be termed a tension series.

Magnesium,
Zinc,
Aluminum,
Cadmium,
Iron,
Cobalt,
Nickel,
Lead,
Mercury,
Silver,
Copper.

A metal anywhere in the above series will tend to precipitate from its salt a metal located lower in the series, for example, zinc will precipitate copper from its salts, etc. A metal at any point in the series, when made an electrode in a cell of battery against a metal lower in the series, serving as the other electrode, will throw off ions in the solution, and thereby become the negative pole. Zinc is the negative pole in almost all cells of battery. The position of a metal in the tension series is of extreme interest to us in the design of primary batteries.

We will close the present chapter by a consideration of the energy of the primary cell based upon a known chemical reaction. If we know the chemistry of a cell of battery we can, by a simple mathematical process, predict what its electromotive force will be. This calculation may be very simple or very complex, depending upon which way we attack the problem. As it has been the aim of the author to avoid the higher mathematics in the present work, we will proceed with a comparatively simple formula. Let us, therefore, select a typical simple cell, look into its chemistry, and predict therefrom the maximum electromotive force which such a cell is capable of giving. This work will take us back into certain of our fundamental principles as introduced in the early portion of the present book and involve Faraday's Law, together with several fundamental units, and the most important constant 96,540. For this purpose of illustration we may do best by selecting the well-known Daniell type of element, or cell. Helmholtz has pointed out that a relationship may be established between the energy

of the chemical process, or, in other words, the chemical energy of a cell, and the electrical energy produced in exchange. It will be seen that under ordinary conditions, most of the energy which could be obtained as the heat of chemical action can be converted into electrical energy and be made to do work as an electric current. If we allow Q to represent the available heat energy, for one gram-equivalent of a compound that enters into chemical combination in a cell, it may be assumed in some cases that an amount of electrical energy equivalent to this heat energy can be obtained from the cell for each gram-equivalent of chemical transfer. In the case of a Daniell cell, the conditions may be represented by the following equation:

$$Cu, CuSO_4 \text{ Solution}; ZnSO_4 \text{ Solution } Zn.$$
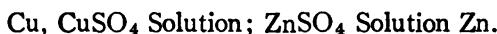
After the cell has been allowed to do work, the condition of affairs may be represented as follows:

$$Zn, CuSO_4 = Cu, ZnSO_4.$$
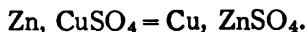
Zinc is therefore dissolved at one pole of the battery, and copper is deposited at the other. The heat value of such a reaction is the difference between the heat of formation of copper sulphate and zinc sulphate in aqueous solution. We have, therefore, $106,090 - 55,960 = 50,130$ calories per gram-equivalent. When 32.5 grams of metallic zinc displace an equivalent of metallic copper from a solution of sulphate of copper, 25,065 calories are set free. We will remember from our study of Faraday's Law that about 96,500 coulombs of electricity are obtained for every 32.5 grams of zinc transported, so if this displacement takes place in a suitable cell we will have 96,500 coulombs of electricity delivered to us. We also learned that the Joule, which is the product of 1 volt by 1 coulomb, is equal to .00024 large Calories or .24 small calories. The electrical energy equal to this number of heat units is $25,065 \div .24 = 104,240$ Joules, therefore $\dfrac{104270}{96500} = 1.08$ volts. This calculation is quite similar in character to the method introduced when we were calculating the minimum E.M.F. required to decompose the gram-molecular weight of any electrolyte when its heat of formation is. known. The Daniell cell, therefore, should give us an E.M.F. of

1.08 volts; and direct measurement of this cell gives us 1.09 to 1.1 volts. It will, therefore, ·be seen how close we may come to the prediction of E.M.F. of a cell when we know its general chemistry.

CHAPTER XVII.

THE SECONDARY CELL.

THE secondary cell in many ways is immensely superior to all forms of primary battery and is of the utmost interest to electrochemists. Unlike the primary cell, it is not susceptible to polarization, or counteraction, resulting from the formation of a film of hydrogen gas upon the surface of the negative electrode. As hydrogen is negative to zinc, for example, a counter electromotive force is set up and the conditions very materially modify the output in the external circuit. Efforts have been made to diminish this in the primary cell by adding depolarizers, which substances combine with the hydrogen liberated at the cathode to form water and are, therefore, oxidizing agents; bichromate of potash is frequently used for this purpose. Whereas the chemistry of the primary cell is well known, that of the secondary cell or storage battery using lead plates and sulphuric acid is far from being understood by chemists. Almost any reversible type of primary cell may be termed a storage battery, because of its reversibility. The original condition of the electrodes and electrolyte may be re-established after a general alteration has been wrought. To give a simple example, let us immerse in a beaker containing dilute sulphuric acid, a stick of chemically pure zinc and a strip of platinum. We have learned from our previous study of the primary cell that no chemical action will take place unless suitable wires are joined to these two metals and brought into contact as in an external circuit. We will then have, as we know, zinc ions being forced into solution and hydrogen ions discharging upon the platinum electrode. An electrical current flows through the wire connector and after a time the electromotive force will be found to fall. An analysis of the dilute sulphuric acid will reveal the presence of zinc sulphate, and we have seen that a certain quan-

tity of hydrogen has escaped as gas.   There will be minute bubbles of hydrogen clinging to the platinum, however, and it is due to this fact that we have the phenomenon of polarization.   By adding potassium dichromate to the dilute acid solution we can effectually prevent the formation of the hydrogen bubbles and maintain a more constant electromotive force.   We can also bring about this depolarization by substituting a rod of copper oxide, for example, for the platinum, which will be reduced to metallic copper by the hydrogen liberated upon its surface.   The cell will then furnish a certain amount of current and do a definite amount of work. There will be found no sulphuric acid left, but a concentrated solution of zinc sulphate instead.   The zinc electrode has been partly consumed.   The zinc, of course, has displaced in the acid the hydrogen, which is set free.   Upon sending an electrical current through the cell in the reversed direction, however, the cell is, incorrectly speaking, recharged.   The "charge" in the present case consists in the deposition of the zinc through the zinc sulphate upon the zinc electrode and the reformation of sulphuric acid. Theoretically speaking, therefore, the only thing lost during the discharge and charge of this particular cell is hydrogen and oxygen gas in the proportion in which they unite to form water.   Such a storage cell is not of a practical nature, however, and has simply been introduced to show the general principle upon which reversible cells depend.   Let us, in our study of the lead-lead-sulphuric acid accumulator, or storage battery, experiment a little, and for this purpose we may best begin by constructing a simple cell, study its practical behavior by charging and discharging it, and examine the plates and electrolyte, by experimental methods, before we look into the theory.   Fortunately, there is no more easily constructed type of cell than a simple storage battery.   For our experimental purpose let us construct a cell, as illustrated in Fig. 113. We may use a rectangular glass cell or large beaker.   A rectangular glass cell is preferable, however, and one about 6 inches high and about 6 inches long by $2\frac{1}{2}$ inches wide will answer our requirements. A rectangular glass jar is to be preferred, for the reason that the lead plates required may be cut in a convenient shape to hang over the mouth of the jar.   These lead plates should be cut from sheet lead, not over $\frac{1}{8}$ of an inch in thickness, and may be provided with

lugs and shoulders, as shown by the diagram of the plate in the center of the illustration. To assemble and charge such a cell we will put into the jar an electrolyte, consisting of one part of concentrated sulphuric acid sp. gr. 1.84 to ten parts of distilled water. The lead electrodes are immersed therein after having been thoroughly cleaned by dipping them into dilute nitric acid, if the lead was not perfectly free from impurities beforehand. A small cell of this character may be easily charged in a very few minutes by connecting it to the motor-generator and supplying about 8 amperes to it under a potential difference of not less than 4 volts. The cell may also be charged by including it in the 110-volt electric lighting circuit
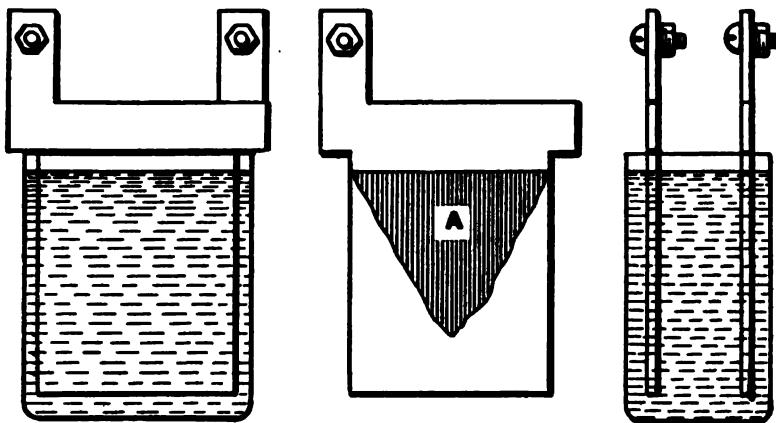
FIG. 113.—Easily Constructed Experimental Secondary Cell.

with a couple of lamps in multiple arc. The primary effect of the electric current is to decompose the water between the lead electrodes. The liberated hydrogen escapes from the cathode, therefore, and the electrolytic oxygen from the anode. The anode plate, if perfectly bright, may be seen to darken under the oxidizing action of the electrolytic oxygen, whereas the cathode assumes a characteristic lead-gray color. For the first few moments, until the two electrodes are reduced and oxidized respectively, there may be no oxygen and hydrogen liberated. The oxygen is oxidizing the metallic lead on the one hand, and the hydrogen is reducing any oxides which may be upon the opposite electrode, on the other hand. After a while, however, bubbles of gas will

appear at the cathode and soon afterwards at the anode, when any further current furnished will not go to charging the cell, but be expended in electrolizing the acidulated water present without any further useful end.

The central diagram in Fig. 113 illustrating the form of lead electrode also indicates in the shaded portion *A*, the manner in which the lead oxide leaves the surface of the oxidized plate on discharge. By referring to Fig. 114, this plate is shown in three
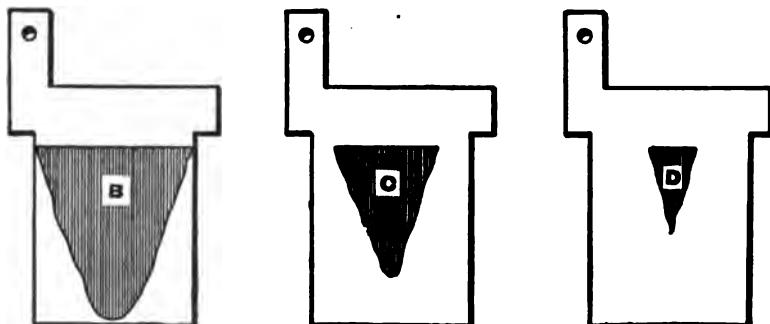
FIG. 114.—Diagram Showing the Appearance of the Positive Plate in Three Stages of Discharge.

stages of discharge. When the cell is completely charged the entire surface of the annode or positive electrode is darkened with the oxide film. Upon discharge, however, the oxide film begins to leave or retreat from the bottom and also the sides of the plate, the diminishing area being depicted by the shaded areas *B*, *C*, and *D* in the figure. It is of interest to note that so long as we have a small area of this oxide film, the E.M.F of the cell is practically constant. This is analogous to the E.M.F. of a primary cell which, as we saw, is a fixed value whether the electrodes are immersed to a large or small extent. The E.M.F., therefore, is again due to the phenomenon of solution tension. If we fully charge a lead-lead-sulphuric-acid accumulator we will find that for a short period of time the cell is capable of giving us an electromotive force of over 2 volts. This E.M.F. has but a very short duration, and is believed to be due to the occlusion of hydrogen by the cathode plate, which, after repeated charging and discharging, assumes a more or less porous and spongy character. We will therefore frequently obtain from storage cells having porous or spongy cathode

plates, an electromotive force as high as 2.4 volts for short periods of time. After we have charged and discharged the experimental cell, with which we are dealing, we will be able to notice this interesting phenomenon. If now we allow the cell to do work by discharging it through a suitable external resistance, interrupting the current momentarily at regular intervals and measuring its E.M.F., or electrical pressure, we will find it to be a trifle under 2 volts and constant up to a certain point, when its value falls abruptly. In other words, a storage battery will yield a good current at a constant voltage for a certain length of time, when the bottom will, so to speak, fall out all at once. By referring to the diagram in Fig. 115,
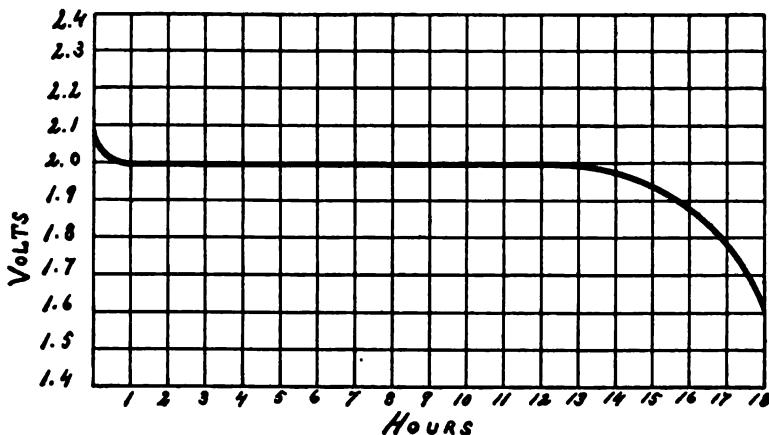
FIG. 115.—Diagram Illustrating the Character of Discharge of a Secondary Cell.

the discharge of a typical storage battery is plotted in the form of a curve for twelve hours. According to this diagram the cell gave a current under a difference of potential of a trifle less than 2 volts, when an abrupt falling off of the electromotive force was noted. For twelve hours, therefore, we may refer to the cell as having a horizontal line of discharge. This is an idealized curve, for in practice this discharge-line is never perfectly horizontal, although very nearly so. We should plot such a curve with our storage cell by reading a delicate volt-meter across the electrodes at, let us say, minute intervals without interrupting the flow of the current in the external circuit. We should now experimentally determine the changes which take place in the electrolyte, that is to say the density

changes that are wrought in the sulphuric acid solution upon charge
and discharge.

During the discharge of a cell of battery the density or specific
gravity of the electrolyte falls, and increases again on charging.   By
knowing the density, therefore, at the point of full charge, and at
full exhaustion, we may learn something of the state of the cell
between those points by specific gravity determinations.   For our
experimental cell a sensitive type of hydrometer may be employed,
as depicted in Fig. 116.   This peculiar construction is the design
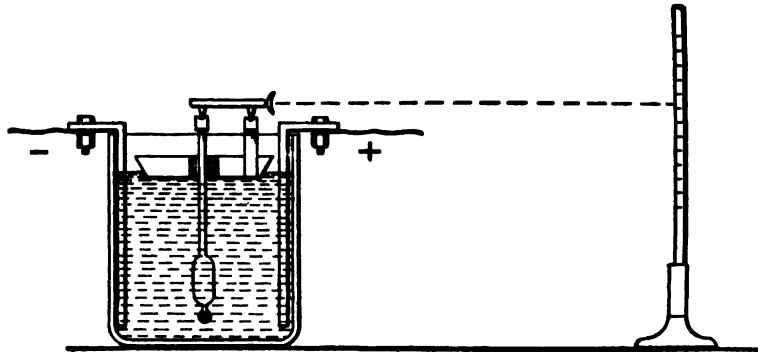
FIG. 116.—Author's Sensitive "Reflecting Hydrometer" for Observing Minute
Density Changes.

of the author as applied to storage-battery study in 1895.   It
consists of an ordinary glass hydrometer equipped with a metal cap
with a V-shape bearing to support a small knife edge on the end
of an aluminum beam.   The other end of this aluminum beam
is equipped with a similar knife edge, which rests in a like V-shape
bearing, mounted upon a standard which is carried by a float.   This
float is provided with a central aperture, not unlike that in a cake
dish through which the stem of the hydrometer passes.   A tiny
mirror is mounted on one end of this aluminum bar, to receive
a beam of light which it reflects upon a scale analogous to that on
the reflecting galvanometer, only in the present case the scale is ver-
tical in place of being horizontal.   It will now be appreciated, from
a glance at the diagram, that the minutest changes in specific gravity
may be noted by the movement of the spot of reflected light upon
the graduated scale.   Another form of specific gravity indicator
which will prove useful in our experimental study of the cell is

illustrated in Fig. 117, which is the design of Mr. J. S. Sellon, and although not so delicate as the one just described, has a useful and practical application for experimental work. We can now charge and discharge our cell, measuring the energy supplied and the energy delivered, examine the electrodes and their behavior, and the
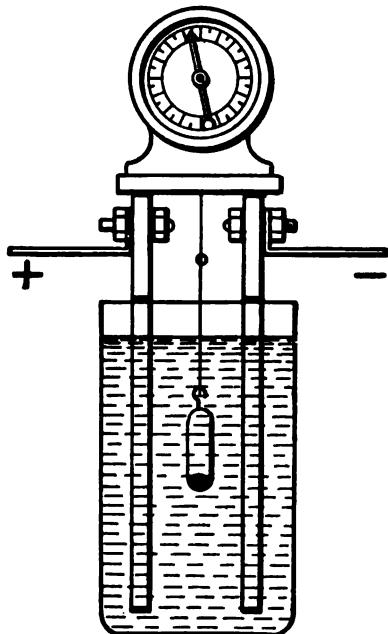
FIG. 117.—Sellon's Design of Hydrometer as Applied to Secondary Cells.

physical changes which take place, such as the density alterations in the electrolyte. What now can be said regarding the theory of this type of battery? It would appear at first sight to be an easy matter when we have such simple elements entering into the construction as pure lead plates and dilute sulphuric acid. Unfortunately, if we attempt to follow theoretically the transformations which takes place in a complete cycle, that is to say the charging and discharging of a secondary cell, we will find that we become lost a number of times in the determination.

Regarding the chemistry of the storage battery in view of the exceedingly difficult chemical problems involved, we will do well to quote from Professor Ayrton's paper on the "Chemistry of Secondary Batteries."

"The physical qualities of the cells are capable of very accurate estimation and investigation. But when you come to attempt to ascertain the chemical changes that occur in the charging and discharging of a storage cell you encounter formidable difficulties. The outsider has no idea of these difficulties. Nothing seems more simple than to determine the chemical changes that take place in either the positive or the negative plate of a storage battery. It is not so in reality. The substances used as actve materials are in the first place mixtures, and the materials obtained at the end of the reactions are also mixtures, and these mixtures are insoluble in any reagent which does not decompose them. They cannot be volatilized; they cannot be subjected to any process of solution and crystallization in order to separate and purify their elements."

There are, however, several theories advanced to account for the charging and discharging of a storage battery, and we would do well to consider some important ones here. Let us first take up the theory of Planté.

The first diagram illustrates the effect of the electric current in the formation of sulphate of lead by the substitution of lead for the hydrogen in the sulphuric acid.

$$-\left|\underset{\underbrace{H_2SO_4 \quad H_2SO_4 \quad H_2SO_4 \quad Pb}_{=2H_2SO_4+PbSO_4}}{\uparrow}\right|+$$
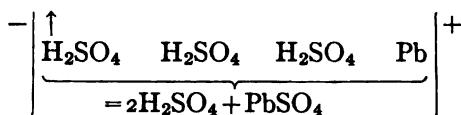
The second diagram shows the production of persulphuric acid by the elimination of a further molecule of hydrogen.

$$-\left|\underset{\underbrace{H_2SO_4 \quad H_2SO_3 \quad O}_{=H_2S_2O_8}}{\uparrow}\right|\underset{PbSO_4}{}+$$
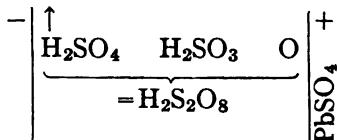
The third diagram shows how the formation of peroxide of lead may take place by the reaction between persulphuric acid and sulphate of lead in the presence of water.

$$-\left|\underset{\underbrace{\begin{matrix}\uparrow\\ \left.\begin{matrix}H_2S_2O_8 \\ 2H_2O\end{matrix}\right\} +PbSO_4\end{matrix}}_{=3H_2SO_4+PbO_2}}{}\right|+$$
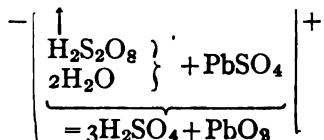
The fourth diagram shows the production of a second molecule of persulphuric acid by the current proceeding from the peroxide-coated anode, and also the decomposition of the persulphuric acid, in the presence of water, which results in the formation of peroxide of hydrogen and the reformation of sulphuric acid.

$$-\left|\begin{array}{c} \uparrow \\ H_2SO_4 \qquad H_2SO_3 \qquad O \\ \underbrace{\underbrace{\qquad\qquad\qquad}_{}}_{\begin{array}{l} H_2S_2O_8 \; \} \\ 2H_2O \quad \} \end{array} = \begin{array}{l} \{ H_2O_2 \\ \{ 2H_2SO_4 \end{array}} \end{array} \; PbO_2 \right|^+$$
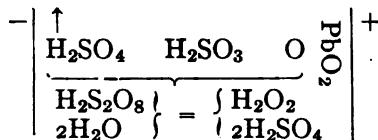
Another theory of the storage battery is as follows: During the discharge of a cell both electrodes are converted into lead sulphate with the abstraction of SO_4 from the electrolyte, which diminishes its specific gravity. The change on the anode or positive electrode is believed to take place in two separate stages: First, the reduction of the peroxide of lead to the monoxide, and then the conversion of the monoxide of lead into the sulphate of lead. When the cell is charged we have the reverse, the sulphate of lead being converted into the peroxide on the positive plate and metallic lead on the negative plate or electrode. According to Treadwell, the generally accepted theory at present is that of the direct formation of lead sulphate at both electrodes, "each molecule of the peroxide is supposed to loose an atom of oxygen, and each atom of spongy lead to gain an atom of oxygen. Two molecules of hydrogen sulphate are thus abstracted from the electrolyte to react with the peroxide or spongy lead, and their places are taken by 2 molecules of water.

$$PbO_2 + H_2SO_4 = PbSO_4 + H_2O + O;$$
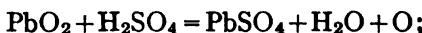
and that for the negative plate is

$$Pb + O + H_2SO_4 = PbSO_4 + H_2O;$$

or, including both reactions in one equation,

$$PbO_2 + 2H_2SO_4 + Pb = PbSO_4 + 2H_2O + PbSO_4.$$
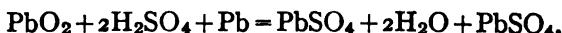
" Thus the final result of the complete discharge of a cell is to form lead sulphate and water by removing sulphuric acid from the electrolyte and depositing sulphate of lead upon each plate.

"The above is, fortunately, a self-limiting process, since the sulphate is a poor conductor. All the peroxide is therefore not acted upon, and at the end of the discharge we have peroxide of lead crystals covered with a coating of sulphate."

So much for the study of conditions. The cell illustrated in Fig. 113 is of the simplest possible type, and, because of the limited electrode area of smooth metallic lead, has but a very low current capacity. When fully charged it will give a current for but a few moments, and for this reason is only adapted for the briefer kind of research and study. This battery can be increased in capacity by roughening the lead plates through the agency of a knurl or other suitable tool.

The battery can also be wonderfully increased in efficiency by not only roughening the anode or positive plate, but by preparing it by filling it in with active material. The practical cells of battery on the market to-day consist of such specially prepared plates, which are termed grids. It would be almost impossible to describe or illustrate the various designs or types of grids intended to meet the rather trying conditions of practice. Perforations of every conceivable shape and size, grooves, mat-work, applications of disks, buttons, chambers, etc., etc., have been devised in order to hold the active material, prepared in numerous ways, to form the positive plate. It would require a special treatise on the storage battery to begin to illustrate and to do justice to the numerous ingenious designs of storage-battery electrodes. Apart from designing a positive plate for maximum efficiency for receiving and holding the active peroxide of lead, we must design an electrode which will not "buckle" under working conditions. Buckling, in storage-battery parlance, is the warping, twisting, and bending of an electrode due to the inequalities in expansion between the active material and the supporting grid or lead work during charge or discharge. With certain types of electrodes this evil is manifested if a battery is charged too quickly or allowed to give up its available current in too short a period of time. Twisting or buckling of the electrode of a storage cell, not only ruins the plates, but interrupts the duty of the cell in a battery because of the short-circuiting which is brought about. A modern storage battery of large capacity is a rather costly thing, and in the hands of incompetent attendants may be easily damaged.

Among the precautions in the care of the storage battery may be mentioned the desirability of having the electrolyte perfectly homogeneous, that is to say, free from strata of different acid concentrations, which will bring about uneven action upon the electrode. Great care should be taken to prevent foreign bodies from falling in between the plates, and to supply pure water to make up for loss due through electrolysis and evaporation. The battery should be charged at either constant voltage or constant current, the current being supplied to the battery under a potential difference only a little higher than that of the battery itself. For example, if we wish to charge ten cells of storage battery in series, a current under a pressure of about 30 volts. will be good practice. In the charging of a single cell, therefore, we should not seek a high-pressure current, but would prefer one with a voltage of about $2\frac{1}{2}$ to 3 volts. In charging the battery, we must know the current density conditions which the battery will stand, that is to say, we should not supply too many amperes per square foot of electrode area. The same question is involved when the battery is allowed to do work, and may be injured as a dynamo may be injured if allowed to discharge through an external circuit of too low a resistance. In the case of the battery we are liable to have buckling due to the heavy current passing, and in the case of the dynamo we are liable to burn out the armature. Too large a charging current, apart from the liability of injuring the battery, is very uneconomical, for a good deal of the electrical energy is transformed into heat. We should, therefore, keep the charging current comparatively low if we seek economy, unless the time of charging is to be counted as one of the elements in cost. Too low a charging current, on the other hand, is also injurious to the cell, for it is found to produce the white sulphate of lead upon the positive plate, instead of the active peroxide, which we seek. Gladstone and Tribe, in their work entitled, "Chemistry of Secondary Batteries," bring out this point as follows:

"If we take two plates of lead in dilute sulphuric acid and pass a current from only one Grove cell, a film of white sulphate, instead of peroxide, makes its appearance on the positive plate, and the action practically ceases very soon. If, however, the current is increased in strength, the sulphate disappears, and peroxide is found in its place."

With a good battery a safe rule to follow is to furnish current to the extent of about 8 amperes per square foot of electrode area. After a battery has been fully charged, oxygen and hydrogen gases are, of course, given off at both electrodes, and the energy which we are furnishing the cell merely goes to the decomposition of water with the setting free of the component gases. This condition is termed "boiling," which does not, as we have seen, refer to any phenomenon due to heat, but merely to the setting free of large volumes of gas. In charging a battery it should never be allowed to fully discharge, about 30 per cent of the available energy being left in every case. The voltage of a storage cell under load should not be allowed to fall below 1.8. When a cell is left to stand without doing work, it should be fully charged.

There are several methods for calculating the capacity of a storage cell in ampere-hours, and as they are purely electrochemical in character should be touched upon before we close the present chapter. The number of coulombs maintained by the consumption of a chemically active substance varies with the change of valence and inversely with the molecular weights of the transforming substance. According to Treadwell, the combustion or liberation of one pound of hydrogen corresponds to 12,160 ampere-hours.

The theoretical current capacity, therefore, in ampere-hours may be figured from the following rule:

"V = the change of valence of the ions;
W = the sum of the molecular weights affected, and
12,160 = the capacity per pound of hydrogen.

$$\text{Then capacity per pound} = \frac{12160 \times V}{W}.\text{"}$$

Regarding lead sulphate, which is the ultimate product at both electrodes, we obtain as the value of the active material by the use of the above formula 40.24 ampere-hours, or 80.48 watt-hours, per pound of lead sulphate, with the lead-lead-sulphuric-acid battery.

For the calculation of electromotive force of storage cells we have the following from "Chemical Theory of Accumulators," by E. J. Wade.

W = the work in joules.

Q = the coulombs of electricity that are passed through the electrolyte.

H = the number of calories liberated by the recombination of a unit weight of one of the decomposed ions.

e = its electrochemical equivalent.

c = its chemical equivalent.

h = the electrochemical equivalent of hydrogen

= .00001038.

J = Joule's coefficient = 4.2

E = the E.M.F. required.

$$W = QE,$$
$$W = QJeH;$$

therefore $E = JeH$

and $e = hc;$

therefore $E = JhcH = 4.2 \times .00001038cH$
$$= .0000436cH.$$

Now, $cH = \dfrac{\text{heat of formation}}{\text{valency}};$

therefore $E = \dfrac{.0000436 \times \text{heat of formation}}{\text{valency}}.$

Since nearly all the battery equations are expressed in terms of the transfer of two atoms of hydrogen, or their equivalent (that is, they are bivalent), and since

$$\frac{.0000436 \times 46000 = 1 \text{ volt}}{2},$$

we have $E = \dfrac{\text{heat of formation in calories}}{46000}.$

CHAPTER XVIII.

ELECTRICITY ·FROM CARBON.

THERE are few problems known to man that promise such a fruitful reward to the advancement of scientific triumph as the one pertaining to the direct conversion of the energy of carbon into electricity. The benefits to be obtained from the solution of this greatest of electrochemical possibilities are practically without words to express. We have on earth but few prime movers when we carefully look into and consider the situation. By prime movers we mean a direct source of energy. Electricity in its dynamic form, and with its applications for purposes of doing work, is but a secondary power. When we consider the question from the basic point of view, we find as tabulated by Joseph Henry in his Scientific Writings, published by the Smithsonian Institution, the following interesting and historic list:

1. Water-power.
2. Wind-power.
3. Tide-power.
4. The power of combustion.
5. The power of vital action.

Continuing, he writes: "To this·list may hereafter be added the power of the volcano and the internal heat of the earth; and, besides these, science at the present time gives no indications of any other. These are denominated primary powers, though in reality, when critically studied, they may all, except the two last mentioned, be referred to actions from without the earth, and principally to emanations from the sun.

" Gravitation, electricity, galvanism, magnetism, and chemical affinity can never be employed as original sources of power. At the surface of the earth they are forces of quiescence, the normal

condition of which must be disturbed before they can manifest power, and then the work which they are capable of performing is only the equivalent of the power which was communicated to them.

"There is no more prevalent and mischievous error than the idea that there is in what are called the 'imponderables' a principle of spontaneous activity. Heat is the product of chemical action, and electricity only manifests power when its equilibrium is disturbed by an extraneous force, and then the effect is only proportional to the disturbing cause. It was for this reason that the existence of electricity remained so long unknown to man. Though electricity is not in itself a source of power, yet from its extreme mobility and high elasticity it affords the means of transmitting power with scarcely any loss and almost inconceivable velocity to the greatest distance. A wave of disturbance starting from the impulse given at the battery will traverse the circumference of the earth in less time than I have been occupied in stating the fact.

"Besides electricity and the principle before mentioned, there are other agents employed between the primary power and the work, namely, the elastic force of steam, of air, and of springs; also various instruments called machines. But these must not be confounded, as they frequently are, with the sources of power. It is not the engine which is the source of motion of the cars, nor yet the steam, but the repulsive energy imparted to the expanding water from the burning fuel."

Through the agency of the steam-engine we obtain mechanical energy which drives the dynamo for the production of electricity. In this system, with its several transformations, the electricity delivered at the terminals of the machine is traced back through the rotating armature with its necessary losses, through the belt or shaft to the engine with its friction and radiation, to the boiler with its many sources of waste, and thence to the grate-bars where heat results from the oxidation of the carbon supported there. It is estimated that only 5 or 6 per cent of the available energy of the carbon is transformed into useful work. If now it were possible within a suitable cell to obtain as a result of the oxidation of carbon the electric current direct without the production of heat, what a majestic discovery would be made!

There is no principle of science standing in our way, and yet

the brightest minds in physical and chemical science have been unable to solve the problem. Heat energy may be transformed into electrical energy, mechanical energy into heat energy, mechanical energy into electrical, etc., etc., etc., without gain or loss, as we learned from the great doctrine of the conservation and correlation of energy. Instead of getting heat energy from carbon we can, as far as existing conditions of science indicate, obtain electricity direct. From the grate-bars, boiler, engine, and dynamo with their combined miserable showing of 5 or 6 per cent energy yield, we may turn for an instant to the primary cell. Here we obtain electricity direct from what we may term the combustion of zinc, by immersing pure zinc and platinum electrodes in dilute sulphuric acid, with a current yield as high as 90 per cent of that theoretically possible. Zinc is too costly a fuel, however, except in special cases and upon a very small scale, and it has been the goal of chemists and physicists to discover a method for obtaining electricity as a direct result of the combustion of carbon or coal. In taking up the consideration of this problem in the present chapter, the writer wishes to warn the student not to confuse thermoelectric deportment with the problem we really have in hand. Many investigators have obtained electricity by using carbon rods in connection with electrodes of different composition immersed in a fused electrolyte, but the source of electricity has been ultimately traced, not to the primary combustion of carbon, but to thermoelectric action. Because of the still existing likelihood of research students going astray in working on this great problem, it may be wise to introduce the subject of thermoelectric action first, and acquaint him with the conditions for its existence before the problem of the direct conversion of the energy of carbon into electricity is dealt with. It was in 1821 that Prof. Seeback of Berlin, noticed that by heating a junction of two metals in a circuit an electric current was produced. The thermoelectric current has been shown by heating the junction between two dissimilar metals of a circuit which surrounds a magnetic needle whereby its direction is noted. If now the source of heat be removed from this junction, and it be cooled by a little ice or some absorbent cotton moistened with ether, an electrical current will be indicated by the magnetic needle but of opposite direction of flow. A thermoelectric couple for experimental purposes may

be easily constructed by joining together two different metals at their lower ends, as indicated in Fig. 118, and leading wires from the upper ends of a galvanometer, or milli-volt-meter. If the lower junction is now heated there will be a current set up, as indicated by the little arrow, from the positive to the negative metal. The electromotive force of this current may be increased by connecting together a number of bars, as shown at the right in this illustration, and heating all the lower junctions and keeping the upper ones
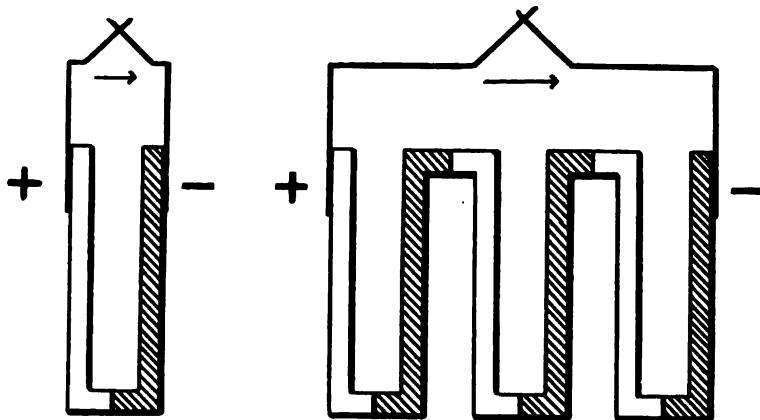
FIG. 118.—Typical Thermoelectric Couplers.

cool. It is upon this plan that the most delicate thermometers, or heat detectors have been devised. Numerous designs of thermo-electric batteries have also been produced, some few of them having proven quite practical in operation, giving as a direct exchange for heat energy energy in the form of electricity. Fig. 119 shows an old form of thermoelectric battery of more scientific interest than practical value. It has been found that a couple made of bismuth and antimony heated at the point of union corresponds very closely in electromotive force to a couple consisting of zinc and copper immersed in sulphuric acid. Couples have been made of many of the available metals, as well as from carbon, and electrical currents obtained under different potentials. At the point of contact between dissimilar conductors of electricity, whether of the metals or of carbon and a metal, electricity is set up in the form of a current when such contact or junction is heated. It is for us to realize this and take

it into account in any work we may do with direct conversion of carbon into electricity. Of all the attempts to reach a solution of this great problem by men with every type of equipment, from the haphazard-try-and-learn character to the research worker with every theoretical equipment, only failure has resulted. One of the great difficulties in the way of solving this problem is in the fact that carbon does not dissolve in suitable electrolytes by the simple throwing off of the positive ions of the carbon.
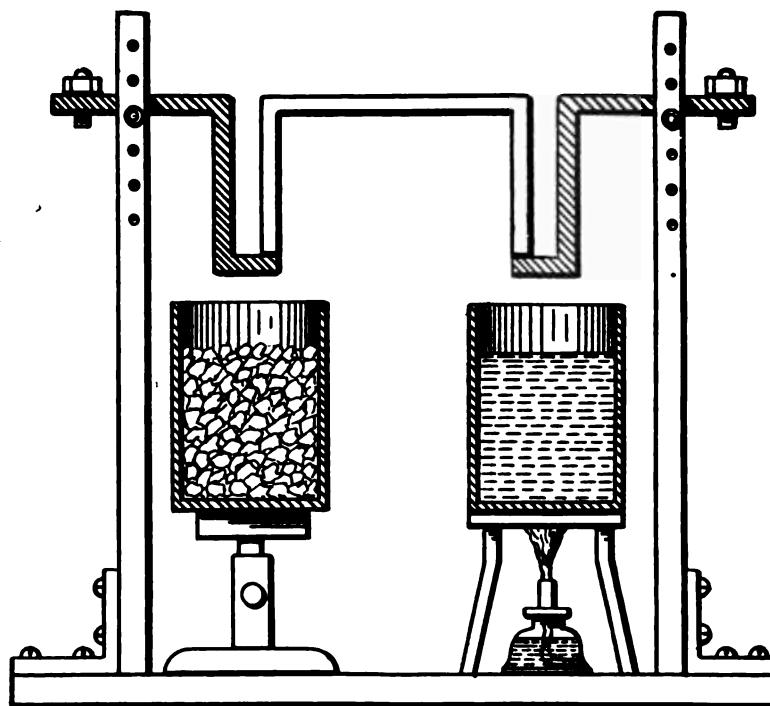
FIG. 119.—Historic Thermoelectric Battery.

As early as 1855 Bacquerel conducted an experiment as illustrated in Fig. 120. A rod of carbon was immersed in a bath of fused nitre contained in an iron or platinum spoon in order to bring about the oxidation of the carbon and the production of the electric current. A galvanometer included in the circuit gave a marked indication. In 1877 Jablochkoff repeated the experiment on a large scale and under certain modified conditions. It will be interesting for us to

note at this time the possible theoretical electromotive force obtainable from a carbon cell when the carbon is oxidized completely to carbon dioxide. From thermochemical data, it has been estimated that a cell in which carbon is completely oxidized to carbon dioxide, the electromotive force obtainable is 1.04 volts. In the majority of experiments which have been made with carbon for the direct production of electricity, the most incomplete data are given. Apart from electromotive force indications on open circuit regarding the deportment of cells, no current data are to be found. One of the most recent carbon cells is that of W. W. Jacques, in which a carbon rod is immersed in fused sodium hydroxide, contained within an iron vessel, heated externally by a furnace; the iron pot serving as a
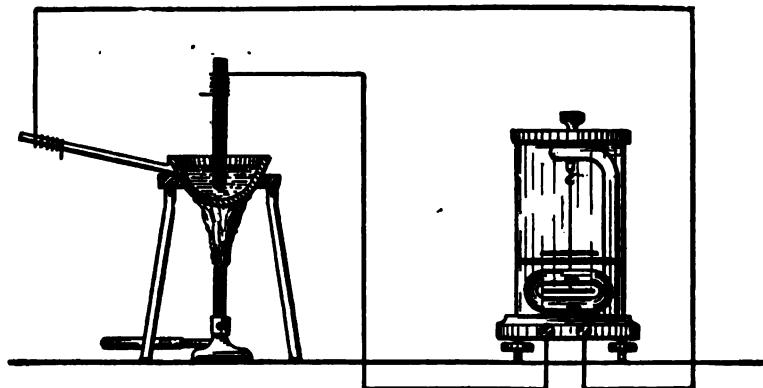
Fig. 120.—Bacquerel's Experiment on the Oxidation of Carbon to Electricity.

positive electrode, while the carbon is the negative. Oxygen is pumped to the bottom of the fused caustic soda through a tube ending in a ring around the lower end of the carbon, the ring being provided with perforations, through which oxygen under pressure escapes and comes in contact with the heated carbon. There is an opening in the cover of this cell whereby the gaseous products of oxidation escape. Of course, air may be pumped into the electrolyte in the place of oxygen, although, for obvious reasons, it is not claimed to be so efficient. According to Jacques, the carbon within is oxidized to carbon dioxide, and the energy produced is given in the form of an electrical current. It was claimed that with a battery of 100 cells a current of about 15 amperes was obtained for 18 hours under

a difference of potential of 90 volts, the consumption of carbon being about 8 pounds. This performance corresponds with an efficiency of about 80 per cent based on that theoretically possible from the weight of carbon oxidized. This calculation does not take into account the energy expended in the form of heat to keep the electrolyte fluid or the energy necessary to pump the air or oxygen through the fused salt. The device is not what has been claimed for it, as it is entirely wrong in principle. Research upon this cell has proven that the electricity does not come at all from the oxidation of the carbon, but from purely thermochemical action. The substitution of other electrodes in the place of the carbon rod gives us practically the same current. If the carbon was oxidized to carbon dioxide gas in the molten caustic soda, we know, as general chemists, that it would be rapidly converted into sodium carbonate, which would ruin it for further usefulness.

Probably the majority of research workers on this problem have immersed a carbon rod against some metal in a strong oxidizing agent, fused nitre for example, in the hope that the oxidation of the carbon would take place with the production of the electric current. In other words, the carbon is brought in direct contact with oxidizing agents. Such a course is manifestly wrong in principle when we look a little into the question of primary cells. If, for example, we wish to obtain electricity by the consumption of zinc, we may do so in several ways. We would undoubtedly obtain a current of electricity if we put a rod of zinc and a strip of platinum in strong nitric acid, but the practice would be a most wasteful one. There would be some electrical current produced, but most of the energy would appear as heat, as the result of the energetic local action of the nitric acid on the zinc. To quote Ostwald upon the subject of electricity from carbon, he says: "The carbon cell of the future must have an oxidizing agent in the place where the carbon is not." To make this statement clear he refers the reader to the experiment where zinc and platinum are immersed in two separate vessels containing a solution of potassium sulphate and separated by a siphon-tube, as illustrated in Fig. 110, Chapter XVI. In order to bring about the economical consumption of zinc in this system we learn that the sulphuric acid must not be added to the beaker containing the zinc, but to that containing the platinum. It is very evident that

if we wish to obtain electricity direct from carbon, as we do from zinc in the primary cell, some electrolyte must be discovered in which carbon will dissolve with the formation of ions. It is to-day uncertain whether or not carbon ionizes in certain solutions under the action of electricity, opinion being divided upon this question. Although the majority of electrochemists do not believe in the ionization of carbon there are certain experiments which tend to show the contrary. Papasogli and Bartoli noticed that the passage of an electric current between carbon electrodes immersed in dilute sulphuric acid was accompanied by certain marked chemical changes. The carbon serving as anode is believed to go into solution for the reason that carbon monoxide and carbon dioxide gases appear as anode products together with the oxygen. Coehn, in working along these lines was able, under certain conditions, to effect the consumption of carbon in dilute sulphuric acid, with the evolution of carbon monoxide and carbon dioxide gases in the proportion of 30 per cent carbon monoxide and about 70 per cent carbon dioxide, an evolution of only about 1 per cent of free oxygen being found. The acid assumed a reddish-brown color believed to be due to the actual dissolution of the carbon. If the electrolysis is allowed to proceed with the carbon as anode, after substituting a platinum cathode, the latter becomes covered with a black deposit. This has been analyzed and found to consist of carbon containing occluded oxygen and hydrogen gases in the proportion in which they combine to form water. Coehn also showed that an electrode of carbon and one of lead peroxide in dilute sulphuric acid produced a constant current until the lead peroxide was reduced to lead, or else the carbon consumed. Of all the attempts to dissolve carbon to obtain the energy of oxidation as electricity, none of them, however, have met with any real success. As pointed out, there are numberless cases of experimental research with the most varied type of cell for the oxidation of carbon, but the electrical data obtainable are exceedingly meagre. In most of the reports of investigators, only a statement of electromotive force is given on open circuits, whereas, we know electrical data pertaining to batteries are useless unless we have together with the electromotive force a statement regarding the number of coulombs the cell will furnish. As many of the cells have been upon the general principle of Jacques, an illustration of one of them

is deemed of interest here. Fig. 121 represents Edison's design, where we have a furnace for heating the iron melting-pot. The cover is of an insulating material and supports the carbon electrode. The electrolyte is chosen from the oxidizing agents, like nitre, for example, or even certain oxides, and, according to Edison, a reduction of the compound takes place, the oxygen combining with the carbon
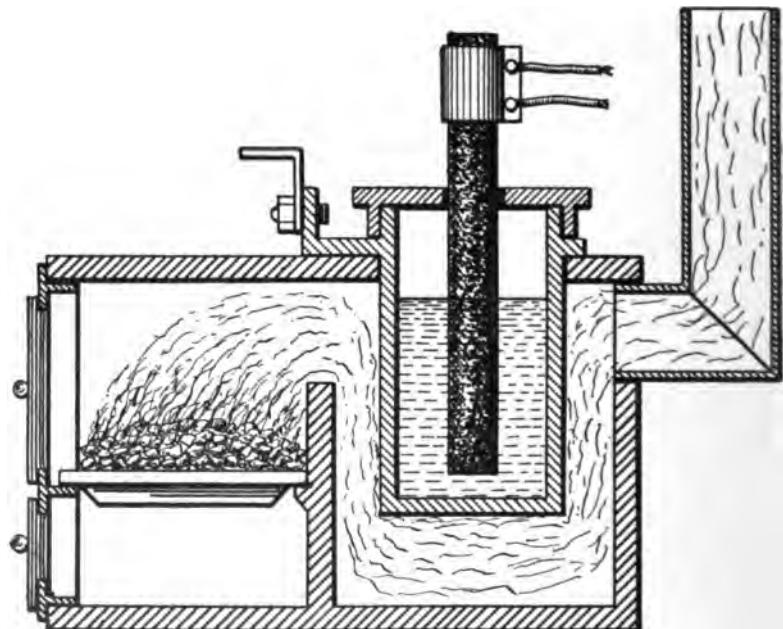
FIG. 121.—Edison's Cell for Obtaining Electricity from Carbon.

in the formation of carbon monoxide, which may be piped off and used for fuel. The residue resulting from the reduction of the oxide may be used over again as the negative agent of the cell. From what we have seen this is entirely wrong in principle, and the electricity obtained is primarily of thermoelectric origin. The problem to-day is one of possible solution, but no practical results have as yet been obtained. To enumerate the various researches upon this important problem would fill a book in itself.

CHAPTER XIX.

USEFUL PIECES OF APPARATUS.

As has been frequently indicated throughout this experimental work, the writer believes that through the introduction of convenient and useful types of apparatus of various kinds, the student often obtains valuable information in the way of suggestions for certain lines of research. It is believed that in many cases the research student receives much benefit from a diagram of apparatus, especially if he possesses ingenuity and has initiative, so to speak, for investigation. There will be many problems in electrochemistry confronting the experimenter, some of which require special types of cells in order that certain conditions of electrolysis may be established. There are, in addition, pieces of apparatus useful in saving time because of their most convenient design and application. For rapidly comparing the conductivities of various electrolytes in small quantities it would be difficult to design a more handy and convenient device than that illustrated in Fig. 122. This cut represents a special form of pipette equipped with a ground glass stop-cock in order that it may easily be held filled by closing the stop-cock. Two simple platinum disks welded to stout platinum wires are sealed into the glass, facing one another, as shown, from opposite sides. Two bent glass tubes fused on the outside of the bulb, are designed to receive the mercury into which protrude the platinum wires passing through the sides of the glass. It will be evident that we can, without danger of breaking off any platinum terminals, make and break electrical connection as often as we see fit by simply immersing our conductors in the tubes and allowing them to dip into the mercury. Another design of cell for conductivity determination is shown in Fig. 123 where we have a special U-shape design of tube with platinum disks, horizontally hung from platinum wires

sealed into the bottoms of glass tubes, which in turn are supported by turned wooden stoppers. These tubes also receive a small quantity of metallic mercury, by means of which contact is made with the electric battery or other source of current.

Fig. 124 shows still another form of cell for conductivity deter-
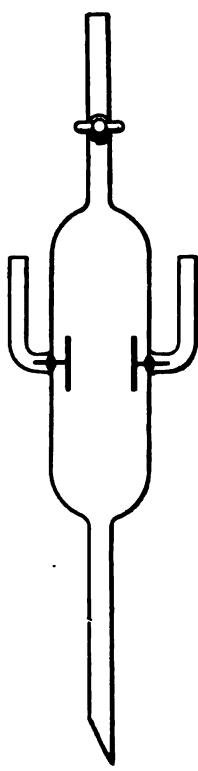
FIG. 123.
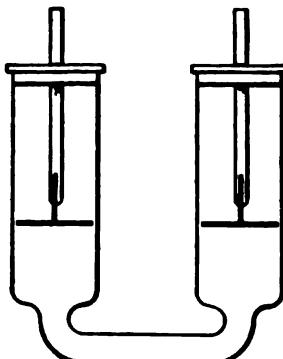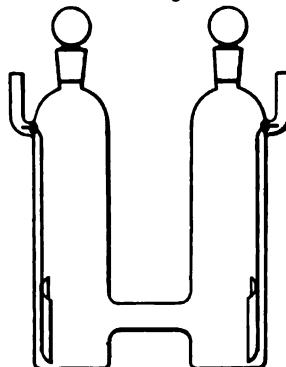
FIG. 122.   FIG. 124.

minations, and has the advantage of allowing for temperature determination being made at both anode and cathode. For this purpose it is only necessary to remove the glass stoppers and insert the thermometers. Such a conductivity cell may be separated into two useful parts by cutting through the glass connecting neck with a sharp file and joining them at almost any distance from one another by inserting a glass tube and rubber connectors. We will then have a piece of apparatus enabling us to obtain anode

and cathode temperatures, to measure absolute velocity of the ions, etc., etc.

Fig. 125 shows a conductivity cell for very accurate determinations, as we have here means not only for making a careful temperature observation and correction, for keeping the temperature constant by immersing the cell within a calorimeter receptical, or glass cylinder, which may be packed with ice.
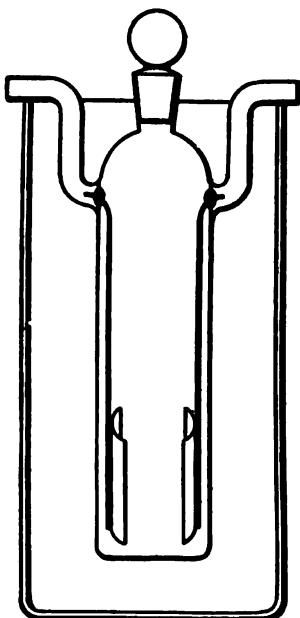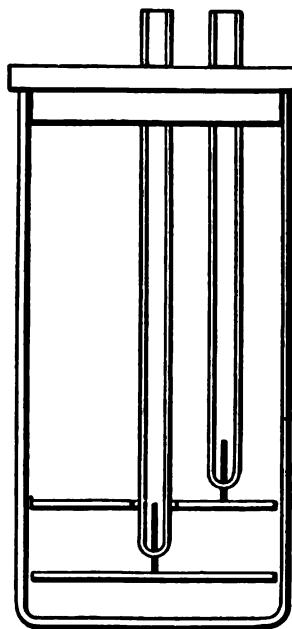
FIG. 125.   FIG. 126.

Fig. 126 illustrates still another type of conductivity cell, which consists of a cylindrical glass vessel containing two large platinum disks fitted loosely within the interior and supported respectively by two glass tubes, through which platinum stems are fused. These tubes, like those in the previous chapter, are designed to be filled, or partly filled, with mercury for the purpose of electrical contact, and the turned wooden top with holes to receive these tubes with a tight fit completes the equipment. The center tube carries an ordinary disk, as shown, suspended by a platinum stem from its center, but the tube on the right has its disk suspended from a point eccentric,

the center of the disk being punched out to allow the middle glass tube carrying the lower disk to pass through. By means of such an arrangement the disks may be brought near together or separated, and apart from serving the purpose of a useful conductivity cell, may be employed also as a very handy and desirable electrolytic rheostat for delicate work. Every electrolytic laboratory should be equipped with a variety of ready decomposition tubes of various shapes and patterns, to be to the electrochemist what the ordinary test-tube is to the general chemist.

Fig. 127 illustrates a simple type of "electrolytic test-tube" of
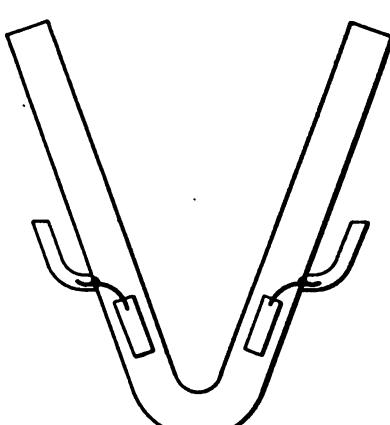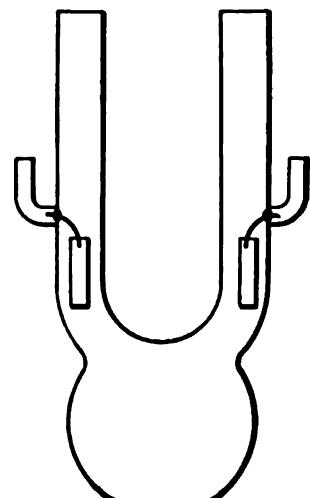
FIG. 127.   FIG. 128.

V shape, equipped with platinum electrodes. Test-tubes of this pattern are exceedingly useful when made from glass, only a few millimeters in diameter and 2 or 3 centimeters in height. There should also be test tubes of this type several centimeters in diameter and 15 or 20 centimeters in height, for the tube is of such general utility that it should be at hand in several sizes.

Fig. 128 is a useful design of cell not only for collecting gases liberated at the electrodes, but also for solids which become detached and fall to the bottom. It consists merely of a U tube equipped with electrodes, and a glass bulb blown upon the lower extremity.

Such a U tube equipped with a bulb serves a useful experimental purpose when employed in the electrolysis of chloride of zinc where it is present in a concentrated aqueous solution. When this is connected with our lamp-bank and the current allowed to flow for a sufficiently long time, the bulb will be filled with beautiful crystals of metallic zinc, whereas, if we use a small U tube the branch-like growth would, instead of breaking off and falling into the bulb, extend across to the positive electrode and short-circuit the cell. It will, therefore, be seen that such a U tube with bulb serves as a receptical for certain electrode products, and therefore fills a useful purpose. The U tube, as depicted in Fig. 129, is of special construction
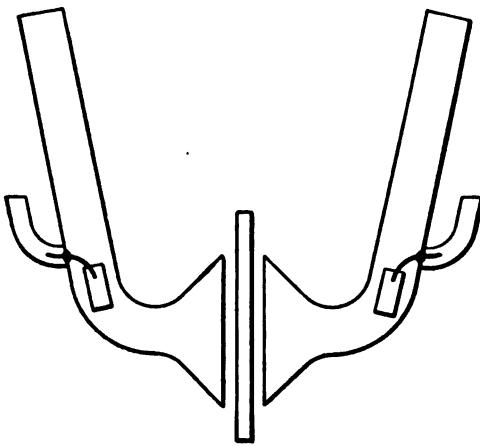
FIG. 129.

and is designed to allow a removable porous partition to be placed between the electrodes. This partition or diaphragm may be of filter-paper, parchment, or even a disk of baked porous material, as the requirements may dictate. The lower ends of the U tube terminate in a bell-shape mouth, over which a clamp may be fixed to draw them into close contact with the separating membrane. Such a piece of apparatus will serve only in special cases, but it has its application in research work and should be included in an equipment.

Fig. 130 illustrates the front and side view of a Hoffmann apparatus, blown from one piece of glass, which deserves a special place of

honor as a device of general utility.' Although small pieces of
Hoffmann apparatus may be ordered from almost any dealer in
chemical ware, when necessary to employ such a cell on a large
scale, it will be convenient and easy to improvise one by using a long
length of glass combustion tubing of large bore.   If a Woulf's bottle
with three wide necks is available, the assembling of a large Hoff-
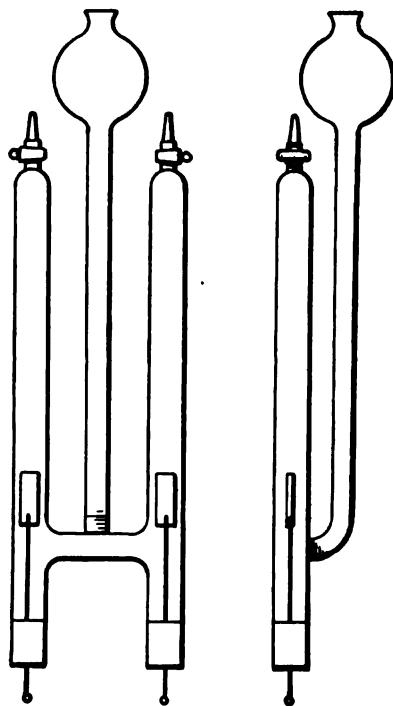
FIG. 130.

mann apparatus is a comparatively simple matter, as will be seen
by any one with aptitude for construction.   In place of the Woulf
bottle a large Hoffmann apparatus for the accumulation of large
quantities of electrode gas may be assembled from the combustion
tubing and a large T joint of glass with rubber connectors.

In closing this chapter a few words relative to the Wenhelt inter-
rupter and aluminum rectifier will perhaps be of interest and value
to us.   Wenhelt's electrolytic interrupter is particularly useful

in connection with the operation of induction-coils, for it serves to take the place of the ordinary vibrator.

Fig. 131 shows a simple form of electrolytic interrupter, which consists simply of a beaker glass containing dilute sulphuric acid, into which is immersed strips of platinum to serve as anode, while the cathode consists of a short piece of platinum wire fused into the lower end of a stout glass tube, bent as shown in the illustration. This tube is filled with mercury, both for the purpose of making an electrical contact with the platinum wire cathode and for conducting away the heat which is generated there. When interposed in an electrical circuit this device serves to rapidly make and break the electric current. The principle of this interrupter is based

FIG. 131.

upon the rapid formation and discharge of bubbles of hydrogen from the platinum point or cathode of the cell which, because of the high current density existing, becomes quite hot. Such an interrupter operates in a most satisfactory manner an induction-coil and other devices where an intermittent current is desired. The adjustment is brought about by varying the distance between the platinum strip anode and the platinum cathode, together with changing the concentration of the sulphuric acid solution. This apparatus is introduced here as of scientific interest from an electrochemical standpoint, in the belief that the student will profit by conducting experiments therewith. Another electrolytic cell of remarkable performance is the aluminum rectifier, which, when placed in series in the circuit of an alternating current, converts the alternating current into an intermittent direct current. This may be regarded as a species of electrical "check-valve," allowing the impulses in one direction to pass through and preventing the impulses in the opposite direction from getting past. Such a rectifier consists simply of a beaker glass containing a suitable electrolyte, into which is immersed an aluminum anode and a platinum cathode. With such an equipment, using disodium phosphate as an electrolyte, a potential difference as high as 300 volts may be established between the electrodes, while only a few hundredths of an ampere will flow through the cell in one direction, because of its high resistance, whereas the resistance is
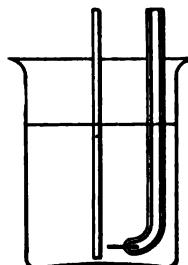
comparatively zero in the reverse direction. Such a cell interposed in an alternating current circuit with only 110 volts pressure is of exceedingly great interest. It is necessary to keep these cells cool by the circulation of water, and for this purpose the aluminum electrode has been employed in the form of a U tube, through which cold water may be made to flow. The principle of the rectifier is believed to be based upon the formation of a non-conducting film upon the aluminum, and which allows a large current to pass through in one direction, but only an exceedingly small one in the other.

CHAPTER XX.

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